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THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*A New Modification of 3 : 4-Dinitrodimethylaniline.*

By Herbert Swann.

During an investigation of the nitration of *m*-nitrodimethylaniline, it was found that by varying the conditions of nitration, a new modification of 3:4-dinitrodimethylaniline was formed. This brings 3:4-dinitrodimethylaniline into line with other nitroanilines, most of which exist in at least two modifications (Hantzsch, *Ber.*, 1910, **43**, 1654).

Romburgh (*Rec. trav. chim.*, 1887, **6**, 250) states that *m*-nitrodimethylaniline is readily nitrated by nitric acid (D 1·2), giving the 3:6- (m. p. 112°) and the 3:4- (m. p. 176°) dinitro-compounds. However, by nitrating *m*-nitrodimethylaniline in certain concentrations of sulphuric acid, and using the requisite quantity of nitric acid to introduce one nitro-group, there results a β-modification of 3:4-dinitrodimethylaniline in addition to the 3:6-dinitroderivative obtained by Romburgh.

β-3:4-*Dinitrodimethylaniline* is an orange-coloured compound melting at 154°. It is possible to convert it into the α-compound (m. p. 176°) by dissolving in concentrated sulphuric acid and diluting the resulting solution with water, when the α-modification separates, melting at 176° after one recrystallisation from alcohol. The β-compound was also readily changed to the α-compound by boiling an amyl-alcoholic solution with a few drops of 80 per cent.

sulphuric acid. On cooling, the α-modification separated in long needles. No method of changing the α- to the β-compound has yet been found.

Nitration of the β-modification with 70 per cent. nitric acid at 30° gives principally 2:4:5-trinitrodimethylaniline (m. p. 196°), which is also obtained by the nitration of 2:5- and α-3:4-dinitrodimethylaniline under the same conditions. The quantity nitrated was too small for the identification of any other trinitro-compound.

The action of more concentrated nitric acid on the above three dinitrodimethylanilines is of interest. Treatment with nitric acid of about 80 per cent. strength results in a simultaneous nitration and oxidation, a trinitromonomethylaniline being formed. A similar oxidation occurs on nitrating dimethylaniline in acetic acid solution, when under certain conditions 2:4-dinitromonomethylaniline is obtained in good yield.

The trinitromonomethylaniline is a yellow, crystalline compound melting at 199°. Its constitution was proved by replacing the mobile *m*-nitro-group by the methoxy-group, when 4:6-dinitromethyl-*m*-anisidine (m. p. 198°) was obtained. The original compound is therefore 2:4:5-*trinitromonomethylaniline*.

EXPERIMENTAL.

Preparation of m-*Nitrodimethylaniline.*

The *m*-nitrodimethylaniline was obtained by the cold nitration of dimethylaniline, as suggested by Nölting and Fourneau (*Ber.*, 1897, **30**, 2931). It was found possible to use much less sulphuric acid in the nitration, thereby facilitating the final neutralisation.

Dimethylaniline (250 c.c.) was dissolved in sulphuric acid (475 c.c.), and the solution cooled in a freezing mixture of ice and salt. The cooled nitrating acid, consisting of 100 c.c. of nitric acid (D 1·5) and 475 c.c. of sulphuric acid, was then added gradually, the temperature being maintained between 0° and 4°. When the whole of the acid had been added, the liquor was poured on ice, and finally diluted with about 20 litres of water, which precipitated the *p*-nitrodimethylaniline. The *m*-nitrodimethylaniline contained in the filtrate was separated by neutralisation with sodium carbonate and crystallised from alcohol, the yield of pure material (m. p. 66°) being about 50 per cent. of the theoretical.

β-3:4-*Dinitrodimethylaniline.*

Fifty grams of *m*-nitrodimethylaniline were dissolved in 500 c.c. of 60 per cent. sulphuric acid, and to this solution (at 20°) 50 c.c.

of 30 per cent. nitric acid were added, the whole being well shaken. After a few minutes the temperature rose to 35°, and the 3:4-dinitrodimethylaniline separated as an orange-coloured, flocculent precipitate. The liquor was diluted with 250 c.c. of water and filtered, when practically the whole of the β-3:4-dinitrodimethylaniline was obtained in the precipitate, the 2:5-isomeride remaining dissolved in the filtrate. The β-3:4-dinitro-compound after one crystallisation from alcohol or benzene melted sharply at 154°, the yield being 60 per cent. of the theoretical.

Found: N = 19·7.

$C_8H_9O_4N_3$ requires N = 19·9 per cent.

By considerable dilution of the filtrate, the 2:5-isomeride separated; after crystallisation from glacial acetic acid it melted at 112°.

α-3 : 4-*Dinitrodimethylaniline.*

This compound was obtained by nitrating *m*-nitrodimethylaniline (1 gram) with 20 per cent. nitric acid (10 c.c.).

It was also prepared by dissolving the β-modification (5 grams) in sulphuric acid (30 c.c.) and gradually diluting the solution with cold water, the temperature not being allowed to rise above 40°. By this method, the β-compound was completely converted into the α-modification, which, after crystallisation from alcohol or acetone, melted at 176°.

Preparation of 2 : 4 : 5-*Trinitromonomethylaniline.*

Twenty grams of 2:5-dinitrodimethylaniline (or α- or β-3:4-dinitrodimethylaniline) were dissolved in 80 c.c. of nitric acid (D 1·40). The temperature was raised to 30°, and 40 c.c. of nitric acid (D 1·50) were quickly added. After a few minutes, a vigorous oxidation took place, as shown by the evolution of nitrous fumes. At this point the solution was cooled rapidly, and, when the oxidation was finished, poured on ice. The precipitate was collected and digested with 500 c.c. of boiling water for several hours to hydrolyse any tetranitrophenylmethylnitroamine which might have been formed. The *m*-nitro-group in 2:4:5-trinitromonomethylaniline is not removed by boiling water. After hydrolysis, the liquid was filtered hot, and the residual solid crystallised from acetone. A moderately good yield of 2:4:5-trinitromonomethylaniline, a bright yellow, crystalline compound melting at 199°, was obtained.

Found: N = 22·8.

$C_7H_6O_6N_4$ requires N = 23·1 per cent.

Nitration of 2:4:5-trinitromonomethylaniline with nitric acid (D 1·50) gives 2:4:5:6-tetranitrophenylmethylnitroamine. Treatment of the boiling methyl-alcoholic solution (2 grams in 100 c.c. of methyl alcohol) with the theoretical quantity of potassium hydroxide (0·5 gram) dissolved in the minimum amount of water furnishes 4:6-dinitromethyl-*m*-anisidine (m. p. 198°), thereby establishing the constitution of the original compound as 2:4:5-trinitromonomethylaniline.

The possibility of the above trinitromonomethylaniline containing a nitro-group as a nitroamine was tested by heating with phenol and sulphuric acid in boiling amyl alcohol, but with negative result.

College of Technology,
Manchester. [*Received, October 22nd*, 1919.]

II.—*The Chloroacetates of* S-*Alkylthiocarbamides.*

By John Taylor.

In a previous communication (T., 1917, **111**, 650), the theory was advanced that salts of *S*-alkylthiocarbamides have a sulphonium structure, $(NH_2)_2C\colon SRX$, where R is an alkyl group and X an acidic residue. The possibility of the existence of ammonium and of carbonium forms, $XNH_3\cdot C(\colon NH)\cdot SR$ and $(NH_2)_2CX\cdot SR$, was considered.

The behaviour of the nitrites and thiocyanates of these compounds points to the improbability of an ammonium structure, whilst the ready ionisation of the salts points to the non-existence of carbonium structure. Occasionally, in the presence of strong acids, a second form of a salt is obtained differing considerably from that separating from a neutral solution. This second form is unstable, being readily converted into the first by recrystallisation from hot water. It was conjectured that this unstable form is of the ammonium type, its instability being paralleled by the instability of the salts of amides.

A study of the chloroacetates of *S*-alkylthiocarbamides, and in particular of the monochloroacetates, confirms the view that the salts have not an ammonium structure.

They are readily prepared by mixing a concentrated aqueous solution of thiocarbamide methyl nitrate or of thiocarbamide benzyl chloride with a solution of the sodium salt of the required acid, when the new compound separates from solution.

To the general rule that a thiocarbamide results from the interaction of a thiocarbimide and a primary or a secondary amine, there is one tolerably well-marked exception, namely, when the radicle of either contains a halogen constituent. In this case, although the primary union may run the normal course, there follows the production of a salt of a cyclic base in which the carbon atom, originally halogenated, is now attached to sulphur, thus:

$$R{\cdot}NCS + NH_2{\cdot}CH_2{\cdot}CH_2Br \longrightarrow R{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH_2Br \longrightarrow$$
$$\begin{array}{l} RN{:}C\text{———}S \\ \quad\ \ | \qquad\quad\ | \\ \quad NH{\cdot}CH_2{\cdot}CH_2 \end{array},HBr,^{*}$$

(Gabriel, *Ber.*, 1889, **22**, 1148). Similarly,

$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NCS + PhNH_2 \longrightarrow$$
$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHPh \longrightarrow$$
$$\begin{array}{l} PhN{:}C\text{—————}S \\ \qquad\ | \qquad\qquad\quad | \\ \quad\ NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br \end{array},HBr^{*}$$

(Dixon, T., 1897, **71**, 617). A similar behaviour is shown by halogen-substituted acylthiocarbimides:

$$CH_2Cl{\cdot}CO{\cdot}NCS + C_7H_7{\cdot}NH_2 \longrightarrow C_7H_7{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}CH_2Cl \longrightarrow$$
$$\begin{array}{l} C_7H_7{\cdot}N{:}C\text{———}S \\ \qquad\quad\ | \qquad\quad | \\ \qquad NH{\cdot}CO{\cdot}CH_2 \end{array},HCl^{*}$$

(Dixon, *loc. cit.*). The same change results when an already formed non-halogenated thiocarbamide has halogen introduced into its molecule:

$$CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2 \xrightarrow{I} CH_2I{\cdot}CHI{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2 \longrightarrow$$
$$\begin{array}{l} NH{:}C\text{———}S \\ \quad\ \ | \qquad\quad | \\ \quad NH{\cdot}CH_2{\cdot}CH{\cdot}CH_2I \end{array},HI^{*}$$

(Dixon, T., 1896, **69**, 25).

Only two exceptions to this rule appear to exist, namely, (1) where halogen is attached to an aromatic radicle, thus the compound $C_6H_4Cl{\cdot}NH{\cdot}CS{\cdot}NH_2$ is quite stable (Losanitsch, *Ber.*, 1872, **5**, 156), and (2) where halogen is part of an unsaturated radicle; thus the compound $CH_2{:}CCl{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$ does not yield a cyclic compound (Henry, *Ber.*, 1872, **5**, 188; Dixon, T., 1901, **79**, 553).

It is clear, from these examples, that there is, in thiocarbamides, a very strong tendency towards the conversion of bivalent into quadrivalent sulphur when there is present a halogenated radicle not already linked to sulphur.

* These formulæ are written as the authors themselves gave them. The present author prefers to represent them as sulphonium compounds.

If thiocarbamide methyl monochloroacetate had an ammonium structure, that is, $CH_2Cl{\cdot}CO_2{\cdot}NH_3{\cdot}C(:NH){\cdot}SMe$, there would follow the formation of a cyclic compound,

$$\begin{array}{l} NH:C\text{———}SMeCl \\ \quad\;\; | \qquad\qquad | \\ \quad NH_3{\cdot}O{\cdot}CO{\cdot}CH_2 \end{array} .$$

Such a union occurs as the initial stage of the formation of thetines.

This compound would have its chlorine highly ionised, it would respond to Andreasch's test for thiolacetic acid (*Ber.*, 1879, **12**, 1385), and, further, the chloroacetate group, being now divided into two parts, could not be displaced wholly by another acid group.

Thiocarbamide methyl chloroacetate, prepared as described, agrees in no respect with these properties. Its aqueous solution does not yield silver chloride on the addition of silver nitrate, no purple colour is observed on applying Andreasch's test, hence the compound does not contain the grouping $\cdot CO{\cdot}CH_2{\cdot}S\cdot$, and, lastly, the picrate is identical with that obtained from thiocarbamide methyl nitrate, consequently the whole of the chloroacetate group has been displaced by the picrate residue.

It is thus highly probable that the chloroacetate group is not attached to nitrogen, and that, since ring closing does not occur, the chlorine forms part of a group already linked to sulphur which is already exerting its full valency, and therefore does not admit of further combination.

The structure of thiocarbamide methyl chloroacetate would appear to be represented by the formula

$$(NH_2)_2C:SMe{\cdot}O{\cdot}CO{\cdot}CH_2Cl,$$

in agreement with that proposed for other salts of *S*-alkylthiocarbamides, and would correspond with its properties as described above.

That the chlorine of the chloroacetate residue would combine with sulphur if opportunity occurred is shown by the fact that, wheu this substance is heated in alcoholic solution with thiocarbamide, *iso*thiohydantoic acid results. This is due to the initial formation of an additive compound of the original substances,

$$(NH_2)_2C:SMe{\cdot}O{\cdot}CO{\cdot}CH_2Cl + CS(NH_2)_2 \longrightarrow$$
$$(NH_2)_2C:SMe{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}SCl:C(NH_2)_2,$$

which readily loses hydrogen chloride. The acid, in turn, decomposes the methyl-ψ-thiourea ester of *iso*thiohydantoic acid, leaving free *iso*thiohydantoic acid,

$$(NH_2)_2C:SMe{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}C(:NH){\cdot}NH_2 \xrightarrow{HCl}$$
$$(NH_2)_2C:SMeCl + CO_2H{\cdot}CH_2{\cdot}S{\cdot}C(:NH){\cdot}NH_2.$$

When thiocarbamide benzyl chloroacetate instead of the methyl compound is combined with thiocarbamide, loss of hydrogen chloride alone follows, and the benzyl-ψ-thiourea ester of *iso*thiohydantoic acid is obtained, showing that the reaction proceeds in the manner suggested.

Attempts to remove hydrogen chloride alone from thiocarbamide methyl chloroacetate by the use of dilute alkali or of pyridine were quite unsuccessful. No indication of the formation of a glycine derivative was observed; the whole of the chloroacetate group was removed and the resulting ψ-thiourea decomposed.

Thiocarbamide and methyl chloroacetate unite additively on long contact in acetone solution. The product is isomeric with the thiocarbamide methyl chloroacetate previously described. There are many points of difference between the two substances; thus the additive compound is readily soluble in water, and the solution is acid, due to the formation of hydrochloric acid. When boiled in alcoholic solution, it loses methyl alcohol, and the hydrochloride of *iso*thiohydantoic acid separates on cooling. With less than one equivalent of sodium hydroxide, both methyl alcohol and hydrochloric acid are lost and *iso*thiohydantoin is obtained. The substance also readily responds to tests for thiolacetic acid.

These reactions are in sharp contrast with those previously described for thiocarbamide methyl chloroacetate, and point to the additive compound being the *hydrochloride* of *methyl* iso*thiohydantoate*, $(NH_2)_2C\colon SCl\cdot CH_2\cdot CO_2Me$. Ethyl chloroacetate combines similarly with thiocarbamide.

Dichloroacetates and trichloroacetates of *S*-alkylthiocarbamides were also prepared. In general properties they closely resemble the monochloroacetates, with the exception that they are inert towards thiocarbamide.

Experimental.

Thiocarbamide methyl monochloroacetate is precipitated when to a concentrated aqueous solution of thiocarbamide methyl nitrate is added an excess of a concentrated aqueous solution of sodium monochloroacetate. On crystallisation from alcohol, it forms prisms, which decompose at about 157°. Its aqueous solution is neutral and furnishes a picrate, melting at 220°, identical with the picrates from other salts of *S*-methylthiocarbamide. The monochloroacetate responds to the usual tests for *S*-methylthiocarbamides; an alkaline solution of lead acetate gives lead mercaptide, and an ammoniacal solution of silver nitrate gives silver mercaptide and silver cyanamide, no silver chloride being formed.

Found: N=15·01, and 100 parts gave 168 parts of silver as AgSMe and Ag_2CN_2.

$C_4H_9O_2N_2ClS$ requires N=15·17 per cent., and 100 parts require 175 parts of silver.

When the solid was heated with one equivalent of pyridine, methyl mercaptan escaped. Addition of one equivalent of *N*-sodium hydroxide to a dilute solution of the substance did not cause a precipitation of methyl-ψ-thiourea. When the alkaline solution was acidified with chloroacetic acid and then evaporated, the original substance was recovered. Attempts were made at various stages to obtain a copper derivative of glycine, but quite unsuccessfully.

Thiocarbamide benzyl monochloroacetate was prepared similarly from thiocarbamide benzyl chloride and sodium monochloroacetate. Water and alcohol each dissolve the substance readily, but it is sparingly soluble in a solution of sodium monochloroacetate. The usual reactions of a ψ-thiourea are given, and it yields a *picrate* which melts at 183°.

Decomposition occurs on heating to 156°.

Found: Cl=13·4; N=10·65.

$C_9H_{11}O_2N_2ClS$ requires Cl=13·63; N=10·74 per cent.

Attempts to prepare sulphonium and ammonium forms of this compound were unsuccessful. Benzyl-ψ-thiourea dissolved in chloroacetic acid gave an uncrystallisable syrup. The ammonium form of thiocarbamide benzyl sulphate, on treatment with an acid solution of sodium monochloroacetate, yielded the same product as the sulphonium form gave when treated with a slightly alkaline solution of the same salt. Both were identical with the compound already described, and decomposed at the same temperature, namely, 157°.

Thiocarbamide methyl monochloroacetate and Thiocarbamide.—Alcoholic solutions of these substances in nearly equivalent proportions (the thiocarbamide in slight excess) were heated together on a steam-bath. After a short time, the liquid, originally clear, became turbid, and a white, amorphous solid separated which contained chlorine, and when heated with an alkaline solution of lead acetate gave, first, lead mercaptide, and, on prolonged heating, lead sulphide. It responded also to Andreasch's test for thiolacetic acid, thus showing the formation of a derivative of *iso*thiohydantoic acid. The mother liquors gave a strong reaction for ψ-thiourea. Analysis of the first product gave no decisive figures and indicated a mixture. After the solid had been further heated with a further quantity of alcohol, the ψ-thiourea reactions became very faint.

The analysis and general properties of the solid now showed it to be rather impure *iso*thiohydantoic acid. The substance chars at about 205° (Found: N=20·1; S=23·1. $C_3H_6O_2N_2S$ requires N=20·9; S=23·88 per cent.).

Thiocarbamide benzyl monochloroacetate and Thiocarbamide. —Combination was effected as in the preceding case. The product, free from chlorine, gave a strong reaction for ψ-thiourea, and responded to the tests for thiolacetic acid. It decomposed on heating to 190°. Analysis showed that the components had united with loss of hydrogen chloride, and that little, if any, further decomposition had occurred. The substance may be regarded as the *benzyl-ψ-thiourea ester* of *isothiohydantoic acid.*

Found: N=18·77; S=20·9.

$C_{11}H_{16}O_2N_4S_2$ requires N=18·6; S=21·3 per cent.

An attempt to prepare the real additive compound by allowing the materials to remain together in cold acetone solution for several days resulted in the isolation of a solid containing Cl=5·7, instead of 10·6 per cent. required by the additive compound.

Thiocarbamide and Methyl monochloroacetate.—Direct addition of these substances was effected by allowing equivalent weights, mixed in acetone solution, to remain for two days. Colourless crystals, which decomposed at 200°, separated from the solution. The crystals readily dissolved in water and gave a strongly acid solution. The *picrate* decomposes at 175°. When the compound was heated with an alkaline solution of lead acetate, no trace of mercaptide was observed, but lead sulphide formed readily. Silver nitrate gave a white precipitate which was soluble in ammonium hydroxide. The ammoniacal solution did not yield mercaptide or sulphide when heated, thus indicating the formation of a silver compound of *iso*thiohydantoic acid. A purple coloration in Andreasch's test proved the presence of the group $\cdot CO\cdot CH_2\cdot S\cdot$. Hence the compound is the *hydrochloride* of *methyl isothiohydantoate.*

Found: Cl=19·4.

$C_4H_9O_2N_2ClS$ requires Cl=19·2 per cent.

On boiling with alcohol, it was hydrolysed to the hydrochloride of *iso*thiohydantoic acid (Found: Cl=23·28. Calc.: Cl=22·88 per cent.). When rather less than one equivalent of sodium hydroxide was added to an aqueous solution of the original compound, prisms, recognised as *iso*thiohydantoin (Found: S=27·39. Calc.: S=27·58 per cent.), separated from solution. The substance decomposed at 220°.

Thiocarbamide and Ethyl monochloroacetate.—These substances

were combined by a similar method to the above. The products separated in glassy, six-sided pyramids which dissolved in water, giving an acid solution. It melts at 107° and decomposes at about 120°.

Found: Cl = 17·54.

$C_5H_{11}O_2N_2ClS$ requires Cl = 17·63 per cent.

Thiocarbamide methyl dichloroacetate was precipitated on mixing concentrated aqueous solutions of thiocarbamide methyl nitrate and sodium dichloroacetate. White crystals were obtained on crystallising the substance from alcohol. The substance showed all the usual reactions of methyl-ψ-thiourea and none of *iso*thiohydantoin. It decomposes at 165°.

Found: Cl = 32·01.

$C_4H_8O_2N_2Cl_2S$ requires Cl = 32·4 per cent.

Heating with even deficit of alkali caused the evolution of mercaptan. No sign of further combination was observed after the substance had been heated for several hours in alcoholic solution with thiocarbamide.

Thiocarbamide benzyl dichloroacetate was prepared similarly. No striking peculiarity was observed in its behaviour. It decomposes at 153°.

Found: N = 10·2.

$C_{10}H_{12}O_2N_2Cl_2S$ requires N = 9·6 per cent.

Thiocarbamide methyl trichloroacetate crystallised in shining leaflets on mixing aqueous solutions of thiocarbamide methyl sulphate and sodium trichloroacetate. Its behaviour was that of an ordinary salt of methyl-ψ-thiourea. Heating with pyridine caused complete decomposition, and on being heated alone it decomposed at 187°. One hundred parts of the substance gave 124·2 parts of silver, whereas 100 parts of $C_4H_7O_2N_2Cl_3S$ require 127·4 parts of silver.

Thiocarbamide benzyl trichloroacetate was prepared similarly. It resembled the preceding compound in appearance and behaviour and decomposed at 150°. An identical product was obtained by heating together benzyl-ψ-thiourea and tricbloroacetic acid.

Found: N = 8·52; Cl = 31·4.

$C_{10}H_{11}O_2N_2Cl_3S$ requires N = 8·45; Cl = 32·3 per cent.

Alcoholic solutions of this compound were heated for several hours with one, two, and three equivalents, respectively, of thiocarbamide, but no indication of the formation of *iso*thiohydantoin

derivatives was observed. The residue from the evaporation of the alcoholic solution also failed to indicate the presence of *iso*thiohydantoin, but reacted freely for ψ-thiourea.

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III.—*The Electroaffinity of Aluminium. Part I. The Ionisation and Hydrolysis of Aluminium Chloride.*

By JAROSLAV HEYROVSKÝ.

ALUMINIUM chloride is a quaternary, strong electrolyte exerting a fourfold osmotic pressure in dilute solutions. In a solution there may exist the ions $AlCl_2^{\cdot}$, $AlCl^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and Cl'. There is no evidence for the existence of complexes, such as $(AlCl_3)_2$; the single molecules seem to possess more affinity for water than for each other.

The cations combine to a certain degree with the hydroxyl ions to form $AlCl_2{\cdot}OH$, $AlCl(OH)_2$, and $Al(OH)_3$; as, however, this hydrolysis does not exceed 3·8 per cent. even in the most dilute solutions concerned, it will first be neglected in considering the dissociation of aluminium chloride.

Let the concentration of aluminium chloride in gram-equivalents per litre be denoted by c, and that of the chloridions resulting from the dissociation be cx (where x is less than 1).

Let the concentration of the $Al^{\cdot\cdot\cdot}$ cations, expressed in gram-cations per litre, be

$$[Al^{\cdot\cdot\cdot}] = c\,.\,y_3\;(y_3<\tfrac{1}{3}),$$

further let

$$[AlCl^{\cdot\cdot}] = c\,.\,y_2\;(y_2<\tfrac{1}{3})$$

$$[AlCl_2^{\cdot}] = c\,.\,y_1\;(y_1<\tfrac{1}{3})$$

and

$$[AlCl_3] = c\,.\,y_0\;(y_0<\tfrac{1}{3}).$$

Then

$$y_0+y_1+y_2+y_3 = \tfrac{1}{3} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$y_1+2y_2+3y_3 = x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We shall first consider how the dissociation would change with dilution if the law of mass action were valid.

We should have:

$$\left.\begin{aligned} cy_0 &= K_0\,.\,cy_1\,.\,cx \\ cy_1 &= K_1\,.\,cy_2\,.\,cx \\ cy_2 &= K_2\,.\,cy_3\,.\,cx \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which gives
$$y_2 = K_2 \cdot cx \cdot y_3$$
$$y_1 = K_1K_2 \cdot (cx)^2 \cdot y_3$$
$$y_0 = K_0K_1K_2 \cdot (cx)^3 \cdot y_3.$$

Substituting in equation (1), we get
$$y_3\{K_0K_1K_2(cx)^3 + K_1K_2(cx)^2 + K_2cx + 1\} = \tfrac{1}{3}$$

hence
$$y_3 = \frac{1}{3\{K_0K_1K_2(cx)^3 + K_1K_2(cx)^2 + K_2(cx) + 1\}} = \frac{1}{3a}.$$

Similarly
$$y_2 = \tfrac{1}{3} \cdot \frac{K_2(cx)}{a},$$
$$y_1 = \tfrac{1}{3} \cdot \frac{K_1K_2(cx)^2}{a},$$
$$y_0 = \tfrac{1}{3} \cdot \frac{K_0K_1K_2(cx)^3}{a}.$$

Since
$$x = y_1 + 2y_2 + 3y_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when c becomes great, x approaches zero, and therefore

y_1 approaches zero
y_2 " "
y_3 " "

And from (1), y_0 approaches $\frac{1}{3}$ (a maximum).

As c approaches zero, x approaches unity; it therefore follows from the above equations that y_3 approaches $\frac{1}{3}$ (a maximum), y_1, y_2, and y_0 approach zero.

We can find the maximum values of y_1 and y_2 as follows:

$$y_2 = \tfrac{1}{3}\frac{K_2(cx)}{a}.$$

Therefore
$$\frac{dy_2}{d(cx)} = \frac{K_2}{3a^2}\{-2K_0K_1K_2(cx)^3 - K_1K_2(cx)^2 + 1\}$$
$$= \frac{K_2}{3a^2y_3}(-2y_0 - y_1 + y_3)$$
$$= \frac{K_2}{3a^2y_3}(x - \tfrac{2}{3}).$$

By equating to zero, we find that y_2 is a maximum when $x = \frac{2}{3}$. Similarly, we may show that

$$\frac{dy_1}{d(cx)} = \frac{K_1K_2cx}{3a^2y_3}(x - \tfrac{1}{3}),$$

and therefore y_1 is a maximum when $x = \frac{1}{3}$.

Summing up,

y_0 is a maximum when c is great and x is small, and a minimum when c is very small and $x = 1$.

y_1 is a maximum when $x=\frac{1}{3}$ and a minimum when c is very great or very small, that is, when $x=0$ or $x=1$.

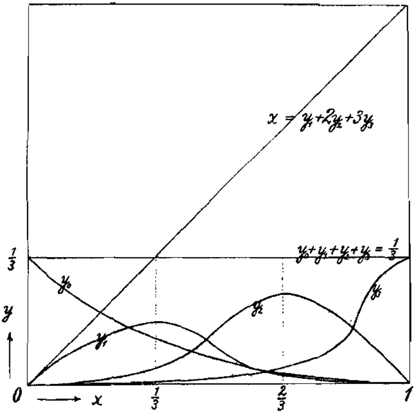
y_2 is a maximum when $x=\frac{2}{3}$ and a minimum when c is very great or very small, that is, when $x=0$ or $x=1$.

y_3 is a maximum when c is very small, that is, when $x=1$, and a minimum when c is very great, that is, when $x=0$.

The changes of y_1, y_2, y_3, and x, corresponding with the gradual splitting into simpler ions on dilution, are plotted in Fig. 1.

This was deduced for an ideal electrolyte obeying the law of

FIG. 1.



mass action. It can, however, be shown that the same mode of dissociation takes place as indicated in Fig. I whatever the law may be so long as it is of the general form

$$\frac{C^{a}_{\text{cation}} \times C^{b}_{\text{anion}}}{C^{p}_{\text{molecule}}} = K.$$

(For van't Hoff's constant, $a=b=\frac{3}{4}p$; for Ostwald's, $a=b=p$.)

Thus, assuming that the indices a, b, c, . . . are in arithmetic progression, we obtain

$$\frac{dy_2}{d(cx)} = d\frac{{}^{n+1}.(cy_2)^{m}}{d(cx)} \cdot \frac{c}{3a^2(cy_2)^{m+1}(cx)^{n+1}}(x-\tfrac{2}{3}),$$

which means that y_2 is a maximum when $x=\frac{2}{3}$, just as in the previous case, and similarly for y_1 and y_3.

The coefficient x, representing the ionised fraction of chlorine, may be determined from the potential of a calomel electrode filled with the respective aluminium chloride solution.

These results, however, would give only the maximal and minimal value of y_3, that is, of the dissociation into $Al^{\cdot\cdot\cdot}$ ions, but no evaluation whatever as to y_1 and y_2.

Further conclusions respecting the $[Al^{\cdot\cdot\cdot}]$ concentration can be drawn from the hydrolysis of aluminium chloride solutions when *solid aluminium hydroxide is present.* Then $[Al^{\cdot\cdot\cdot}].[OH']^3=K$, the concentration of $[OH']$ being determinable by the potential of a hydrogen electrode.

To evaluate the remaining ionic concentrations, specific conductivities of aluminium chloride solutions must be considered.

Measurements of Electromotive Force.

Measurements of cells of the type

$$Hg \mid \text{calomel solution of } AlCl_3 \mid H_2(Pt)$$

were made with all precautions in the manner described by Tolman and Ferguson (*J. Amer. Chem. Soc.*, 1912, **34**, 232) and Acree (*Amer. Chem. J.*, 1911, **46**, 585, 621, 638), using platinised glass electrodes. Readings on the potentiometer could be made to a tenth of a millivolt.

In order to examine the reproducibility of the electrodes used, the cell was filled with 0·100N-hydrochloric acid. The *E.M.F.* at 18° and 760 mm. was found to be constant for three days at 0·3958±0·0003 volt.

The mercury used was purified and twice redistilled. The hydrogen was passed through alkaline permanganate and lead nitrate solutions, and was finally bubbled through the same solution as was being measured in the cell.

The aluminium chloride was purified by precipitation three times from solution by means of hydrogen chloride, and the solutions were kept at 25° in bottles, the corks of which were covered with paraffin.

The cell was kept in a thermostat at 25°, and the readings were repeated after three or four weeks. The effect of barometric change was much less than the variations due to experimental errors, which became appreciable in dilute solutions. Two hydrogen electrodes were used simultaneously dipping into the same solution; they did not differ by more than 0·5 millivolt.

In this way, the following results were obtained for the cell:

$$+Hg \mid (Hg_2Cl_2 \text{ solid}) \; AlCl_3 \text{ solution} \mid H_2(Pt) -$$

Concentration of $AlCl_3$ in gram-equiv. per litre.	*E.M.F.* observed at different times.				Mean *E.M.F.* in volt.
2·29	0·3739,	0·3735	0·3725,	0·3725	0·373
0·368	0·4810,	0·4810	0·4808,	0·4807	0·481
0·0184	0·6000,	0·6005	0·5930,	0·5924	0·595
0·0092	0·6190,	0·6186	0·6170	—	0·618
0·00613	0·632	—	0·634	—	0·633
0·0046	0·639,	0·646	0·643,	0·641	0·643
0·00306	0·659,	0·658	0·661,	0·655	0·658

In other experiments, the aluminium chloride solutions were shaken with precipitated aluminium hydroxide for several weeks previous to being introduced into the cell. With these solutions, the following results were obtained:

Concentration of $AlCl_3$ *solutions in* gram-equiv. *per litre.*	*E.M.F. observed at different* times.				*Mean E.M.F. in volt.*
2·88	0·4221,	0·4225	0·4218	—	0·4222
0·934	0·4940,	0·4934	0·4939,	0·4934	0·4937
0·1845	0·5351		0·5359		0·5355
0·0675	0·5623		0·5614		0·5620
0·0337	0·5804		0·5818,	0·5807	0·5813
0·02134	0·5965,	0·5980	0·5981,	0·5996	0·5984
0·01067	0·6147,	0·6158	—	—	0·6150
0·00675	0·6376	—	0·6360,	0·632	0·635
0·00213	0·6685	—	0·6667		0·668

In order to find the potentials of the single electrodes, the aluminium chloride–calomel electrodes were compared with normal and tenth-normal calomel electrodes at 25°. Saturated, half-saturated, and quarter-saturated potassium chloride solutions were used successively as intermediate solutions and the values extrapolated. This method of eliminating the liquid potential was found to be much more trustworthy than the use of potassium nitrate or ammonium nitrate solutions. All glass tubes were at least 0·5 cm. wide, and no glass taps were used.

The following values were found for the potential π_N of the electrode.

$Hg \mid (Hg_2Cl_2)AlCl_3$ solution, taking the normal calomel electrode as zero:

Quarter, half, and fully saturated potassium chloride solution as intermediate solution.

Concentration of $AlCl_3$.	*P.D.* against *N*-calomel electrode.			*P.D.* against *N*/10-calomel electrode.			π_N extrapolated.
2·29	−0·0090,	−0·0114,	−0·0137	−0·0615,	−0·0625,	−0·0664	−0·0140
0·368	+0·0294,	0·0282,	0·0278	−0·0249,	−0·0252,	−0·0267	+0·0273
0·0409	0·0766,	0·0768,	0·0772	+0·0238,	0·0238,	0·0234	+0·0772
0·0184	0·0970,	0·0976,	0·0978	0·0444,	0·0444,	0·0444	+0·0985
0·0092	0·1174,	0·1168,	0·1155	0·0636,	0·0634,	0·0633	+0·1150
0·00613	*0·1257,*	*0·1255,*	*0·1253*	*0·0721*	—	—	*+0·1250*
0·00460	0·1352,	0·1328,	0·1320	—	—	—	+0·1320
0·00306	—	0·1420,	0·1420	0·0868,	0·0870,	0·0880	+0·1420

Similarly, the values of π_N of calomel electrodes filled with aluminium chloride solutions saturated with aluminium hydroxide were obtained:

Concentration of $AlCl_3$.	*P.D.* against *N*-calomel electrode using quarter, half, and fully saturated potassium chloride solution.			π_N extrapolated.
2·88	−0·0105,	−0·0132,	−0·015	−0·017
0·934	+0·0106,	0·0092,	0·0076	+0·007
0·0675	+0·0721,	0·0720,	0·0710	+0·070
0·00675	+0·1185,	0·1180,	0·1172	+0·117

For the calculations of conductivities, Jones' data (*Carnegie Inst. Publ.*, No. 170), which agree with those of Ley (*Zeitsch. physikal. Chem.*, 1899, **30**, 206), were used.

Molecular conductivity at 25°.	Dilution *v* 1 mol. in *v* litres.	Molecular conductivity at 25°.	Dilution *v* 1 mol. in *v* litres.
193·51	4	341·24	512
220·86	8	360·56	1024
265·12	32	381·44	2048
308·80	128	398·79	4096

Calculation of Dissociation.

The single potentials, π_N, were plotted against $\log c$, and the values of π_N for use in the following calculations were taken from the smooth curve.

The concentrations of chloridions were found in the following way. If π_N were the potential of a calomel electrode in a given aluminium chloride solution, then the concentration of a potassium chloride solution in which the calomel electrode had this same potential, π_N, was found from the curve showing the relation between the potential of a calomel electrode and the logarithm of the concentration of potassium chloride. It was assumed that the concentration of chloridions in these two solutions was the same,

and the absolute value of the chloridion concentration was then calculated from measurements of the conductivity of potassium chloride solution. The following values of π_N for calomel electrodes in potassium chloride solutions were used (Abegg, Auerbach, and Luther, *Abhandl. Bunsen Ges.*, No. 5):

π_N of	N-	calomel electrode	at	25° =	0·000	volt
,,	$N/10$-	,,	,,	,,	0·0541	
,,	$N/100$-	,,	,,	,,	0·1087	
,,	$N/1000$-	,,	,,	,,	0·164	

Column 3 (table I) was calculated in this way. From this, the ratio $\frac{[Cl']}{c} = x$, column 4, was obtained.

For example, in an $0·0092N$-solution of aluminium chloride the potential of a calomel electrode is equal to the potential of a calomel electrode in potassium chloride solution, for which $\log c = \bar{3}·9114$, that is, $0·008155N$. This, being ionised to the extent of 94·6 per cent., has $[Cl'] = 0·007715$, which must be identical with the concentration of chlorine ions in au $0·0092N$-solution of aluminium chloride. Hence $x = \frac{[Cl']}{C} = 0·8381$.

The $[Cl']$ was not calculated directly from the formula

$$\pi = -0·0591 \log_{10}[Cl'],$$

because second-class (anionic) electrode potentials do not agree exactly with the values calculated from conductivity data, possibly due to the formation of complex mercury ions.

Hydrogen electrode potentials, however, were found to vary strictly according to the formula $\pi = -0·0591 \log_{10} C_H$, when the *concentration of hydrogen ions, C_H, is determined from conductivity* (Bjerrum, *Zeitsch. physikal. Chem.*, 1905, **53**, 428; 1907, **59**, 341).

Thus column 7 (table I) was calculated from the potential of hydrogen electrode, π_H (referred to the normal potassium chloride–calomel electrode as zero), the difference of the two normal electrodes having been taken as 0·2837 volt.

The ratio, $\frac{C_{H^\cdot}}{c}$ (column 8), shows the degree of hydrolysis, h. For example, the potential of a hydrogen electrode in $0·0092N$-aluminium chloride solution is $-0·5037$ volt.

TABLE I.

1	2	3	4	5	6	7	8	9
c = concentration of $AlCl_3$ in gram-equivalent per litre.	$\log_{10} c$.	[Cl′].	x.	x'.	π_H in volt.	[H˙].	$\frac{[H^{\cdot}]}{c} = h$.	Maximum y_0.
0·00306	3·48572	0·00267	0·873	0·835	0·5162	0·000116	0·0378	0·055
0·00460	3·66276	0·00395	0·859	0·829	0·5118	0·000138	0·0300	0·057
0·00613	3·78746	0·00522	0·851	0·825	0·5080	0·0001603	0·0262	0·058
0·00920	3·96400	0·00772	0·838	0·817	0·5037	0·0001897	0·0206	0·061
0·01585	$\bar{2}$·2000	0·01295	0·817	0·803	0·4980	0·0002275	0·0143	0·065
0·02291	$\bar{2}$·3600	*0·01848*	*0·806*	*0·794*	*0·4937*	*0·000280*	*0·0122*	*0·067*
0·03162	$\bar{2}$·5000	0·0251	0·793	0·783	0·4900	0·000323	0·0102	0·072
0·05012	$\bar{2}$·7000	0·0387	0·772	0·764	0·4850	0·000393	0·00783	0·078
0·1585	$\bar{1}$·2000	0·1149	0·725	0·721	0·4710	0·000659	0·0042	0·093
0·480	$\bar{1}$·6810	—	0·666	0·664	—	—	0·00362	0·112
0·631	$\bar{1}$·800	—	—	0·646	—	—	0·00360	—
1·2359	0·092	*0·7550*	*0·611*	*0·607*	*0·4190*	*0·00520*	*0·00421*	*0·131*
2·290	0·3598	1·310	0·572	0·564	0·3870	0·01807	0·00789	0·145

$$\text{Hence } 0{\cdot}0591 \log_{10} C_{H^{\cdot}} = -0{\cdot}5037 + 0{\cdot}2837 = -0{\cdot}2200 \text{ volt}$$

$$\log_{10} C_{H^{\cdot}} = -\frac{0{\cdot}2200}{0{\cdot}0591} = -3{\cdot}722 = \bar{4}{\cdot}278$$

from which $C_{H^{\cdot}} = 0{\cdot}0001897$

$$h = \frac{C_{H^{\cdot}}}{c} = 0{\cdot}0206 = 2{\cdot}06 \text{ per cent.}$$

As the hydrolysis in the solutions used is less than 3·8 per cent., we may neglect the concentrations of cations such as $Al(OH)_2^{\cdot}$ and $Al(OH)^{\cdot\cdot}$, and assume

$$[Al^{\cdot\cdot\cdot}] + [AlCl^{\cdot\cdot}] + [AlCl_2^{\cdot}] + [H^{\cdot}] = [Cl'],$$

or

$$3cy_3 + 2cy_2 + cy_1 + C_{H^{\cdot}} = cx,$$

from which it follows that

$$3y_3 + 2y_2 + y_1 = x - h = x'.$$

The values of x' (column 5) are obtained by subtracting the numbers in column 8 from those in column 4.

This number, x', limits the value of y_3, the maximum value of which can be $\frac{x'}{3}$ (when no other cations exist in solution, in which case, also, y_0 is at a maximum). The *minimal* value of y_3 is $x' - \frac{2}{3}$ in the case when most of the $AlCl^{\cdot\cdot}$ cations are formed. In this way, columns 9, 10, and 11 were obtained.

Considering the difficulty with which second and third ionic charges are acquired, the minimal values of y_3 are more probable.

TABLE I.

10	11	12	13	14	15	16	17	18	19	20
Maximum. y_3.	Minimum. y_3.	Equivalent conductivity. λ_c.	A.	$\frac{A}{x'}$	π_H' in volt.	$[H^{\cdot}]'$.	$a = \frac{[H^{\cdot}]'^3}{[H^{\cdot}]^3}$	y_3.	y_2.	y_1.
0·278	0·168	120·2	40·9	49·0	as π_H.	as $[H^{\cdot}]$	1	0·180	0·142	< ·01
0·276	0·162	116·3	40·7	49·3	—	—	—	0·175*	0·153*	—
0·275	0·158	113·7	40·5	48·93	—	—	—	0·170*	0·161*	—
0·272	0·150	110·3	40·0	48·74	—	—	—	0·160*	0·169*	—
0·268	0·136	106·0	39·0	49·18	0·503	0·000187	0·811	0·146	0·178	0·009
0·265	*0·127*	*103·0*	*38·1*	*47·88*	*0·4985*	*0·000207*	*0·761*	*0·137*	*0·187*	*0·009*
0·261	0·116	100·0	36·9	46·8	0·498	0·000227	0·727	0·131	0·188	0·014
0·255	0·097	95·3	34·5	45·18	0·4955	0·000260	0·684	0·123	0·19	—
0·240	0·054	83·3	27·5	38·14	0·490	0·000323	0·418	0·075	0·2	0·10
0·221	0	—	—	—	0·487	0·000392	0·248	0·044	0·2	0·13
—	—	—	—	—	—	—	—	—	—	—
0·202	0	—	—	—	—	—	—	—	—	—
0·188	0	—	—	—	—	—	—	—	—	—

* These values are found by extrapolation.

In order to obtain more precise numbers, conductivity results have to be included. Denoting by M_1, M_2, M_3 the mobilities of cations carrying the total charge of one faraday each, that is, of the ions $AlCl_2^{\cdot}$, $\frac{1}{2}AlCl^{\cdot\cdot}$, $\frac{1}{3}Al^{\cdot\cdot\cdot}$ respectively, and taking the mobilities of chloridion as 75·0 and that of hydrion as 365·0 at 25°, the equivalent conductivity of a solution of aluminium chloride, λ_c, is

$$\lambda_c = 3y_3M_3 + 2y_2M_2 + y_1M_1 + x\,.\,75 + h\,.\,365,$$

from which A is obtained (column 13), as

$$A = 3y_3M_3 + 2y_2M_2 + y_1M_1 = \lambda_c - x\,.\,75 - h\,.\,365.$$

The total charge carried by the three different cations $AlCl_2^{\cdot}$, $AlCl^{\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$ is cx' faradays, and as they contribute to the conductivity, the amount A, the mean equivalent mobility for one cation is $\frac{A}{x'}$. Since this value, as is evident from column 14, approaches 49·2 as the solution becomes very dilute and all the cations become $Al^{\cdot\cdot\cdot}$, the number 49·2 has been taken as the most probable equivalent mobility of $Al^{\cdot\cdot\cdot}$.

In order to evaluate the other unknowns, more relations are necessary. These are obtained from the most dilute solutions where the third stage of hydrolysis is reached, and are supposed to be in equilibrium with solid aluminium hydroxide, the values of π_H in pure aluminium chloride solutions and in those saturated

with aluminium hydroxide (column 15) coinciding in concentrations less than $0{\cdot}01N$. In these solutions,

$$[OH']^3 . cy_3 = K_{Al(OH)_3},$$

where $K_{Al(OH)_3}$ denotes the ionic product of aluminium hydroxide. *Its value lies, according to the values of* y_3, between $1{\cdot}0$ and $1{\cdot}5 \times 10^{-33}$ (the ionic product of water being taken as 10^{-14}).

Further, in most dilute solutions y_0 is negligible, so that

$$y_1 + y_2 + y_3 = \tfrac{1}{3}.$$

Solving these equations for the three most dilute solutions, we get

$$K_{Al(OH)_3} = 1{\cdot}06 \times 10^{-33}\ M_2 = 47{\cdot}0.$$

$$M_3 = \text{about } 30,$$

and the different values of y_1, y_2, and y_3 are given in columns 18, 19, 20.

The values of y_3 in concentrations greater than $0{\cdot}01N$ were calculated from the ratio of hydrion concentrations $[H^{\cdot}]'$ in solutions of aluminium chloride saturated with aluminium hydroxide to $[H^{\cdot}]$ in solutions of aluminium chloride alone. In column 17 a denotes the ratio of the cube of $[H^{\cdot}]'$ obtained from the potential π_H' of the hydrogen electrode in these solutions to the cube of $[H^{\cdot}]$ in aluminium chloride solutions.

Conclusions.

Progressive Hydrolysis.—In solutions below $0{\cdot}01N$, the third stage of hydrolysis exists,

$$AlCl_3 + 3HOH = Al(OH)_3 + 3HCl,$$

or the ionic reaction

$$Al^{\cdots} + 3OH' \longrightarrow Al(OH)_3.$$

For the second stage, having the ionic reaction

$$AlCl^{\cdot\cdot} + 2OH' \longrightarrow AlCl(OH)_2,$$

the expression

$$\frac{cy_2 . K_w^2}{[H^{\cdot}]^2 . [AlCl(OH)_2]},$$

should be constant. Here K_w denotes the ionic product of water.

Similarly for the first stage, the expression

$$\frac{cy_1 . K_w}{[H^{\cdot}] . [AlCl_2OH]}$$

should be constant.

These relations cannot, however, be tested, as the concentrations of $AlCl(OH)_2$ and $AlCl(OH)_2$ are not known with sufficient accuracy.

Since the base $AlCl_2OH$ containing two chlorine atoms is prob-

ably weaker than the base $AlCl(OH)_2$ having one more chlorine atom in place of hydroxyl, the slight increase of hydrolysis in the most concentrated solutions (minimum in 0·5*N*-aluminium chloride solution; see Fig. 2) might be interpreted as due to first-stage hydrolysis.

A similar minimum of hydrolysis in the most concentrated solutions was found by Kablukov and Sachanov (*Zeitsch. physikal. Chem.*, 1909, **69**, 419) in the hydrolysis of aluminium bromide at 25° and by Bruner (*Zeitsch. physikal. Chem.*, 1900, **32**, 133) in the hydrolysis of aluminium chloride at 40°.

The determination of hydrolysis by means of hydrogen electrode potentials has been made by Denham (T., 1908, **93**, 41), who obtained for aluminium chloride solutions ranging from 0·19 to 0·024*N*, values of the potential of the electrode about 20 millivolts lower than those observed by the author. He therefore found three times more hydrolysis. In his experiments, the liquid potential was eliminated by means of a concentrated solution of ammonium nitrate, the solutions being allowed twenty-four hours to come to equilibrium.

The hydrolysis of aluminium salts seems to be influenced by the mode of dissolution. For example, if the solution is raised to a temperature above 25°, it does not necessarily return to the same condition at 25° as it was before (Jones, *loc. cit.*). Moreover, a slight excess of hydrochloric acid in the dry salt would cause too great an acidity, and any adjustment of the equilibrium takes place very slowly. This difficulty in attaining equilibrium, if once disturbed, seems to be due to the presence of colloidal aluminium hydroxide, which exhibits the phenomenon of ageing, showing marked insolubility when not in the nascent state. The solutions must be therefore prepared and kept so far as possible at the same temperature. Kablukov and Sachanov's results (*loc. cit.*) for the hydrolysis (at 25°) of aluminium bromide, calculated from *E.M.F.* measurements, are very close to the values given in this paper.

The Heat of Ionisation of Aluminium Hydroxide.—Kulgren (*Zeitsch. physikal. Chem.*, 1913, **85**, 466) measured very accurately the hydrolysis of aluminium chloride at 85° and 100°. From his results, and from the values given in Fig. 2 (curve *h*), the heat of ionisation of aluminium hydroxide can be obtained in the following way.

The degree of hydrolysis of aluminium chloride at the dilution $v=512$ is 4·7 per cent. at 25°, 34·09 per cent. at 85°, and 47·68 per cent. at 100°. Since at this dilution the third stage of hydrolysis exists, the heat of ionisation of the reaction,

$$Al^{\cdots} + 3OH' \longrightarrow Al(OH)_3 \text{ solid},$$

can be calculated from the data given above by means of van't Hoff's isochore.

Thus, considering the equilibria at two temperatures, T and T'

$$\frac{[Al(OH)_3].K}{[Al(OH)_3]'.K'} = \frac{[Al^{\cdots}].[OH']^3}{[Al^{\cdots}]'.[OH']'^3} = \frac{[Al^{\cdots}].K_w^3.[H^{\cdot}]'^3}{[Al^{\cdots}]'.K'^3_w.[H^{\cdot}]^3}.$$

Further, at the same dilution, $v = 512$, the concentrations of the $Al^{\cdots}$ ions can be taken as equal to the non-hydrolysed portion in solution, and since at this great dilution some solid aluminium hydroxide will certainly have separated out, we can write:

$$\frac{[Al(OH)_3].K}{[Al(OH)_3]'.K'} = \frac{K_{Al(OH)_3}}{K'_{Al(OH)_3}} = \frac{1-h}{1-h'}.\frac{K_w^3}{K'^3_w}.\frac{h'^3}{h^3},$$

where h denotes the fraction hydrolysed and $K_{Al(OH)_3}$ and $K'_{Al(OH)_3}$ are the solubility products. Substituting in van't Hoff's formula we get:

$$Q = R\frac{T.T'}{T-T'}\log\frac{1-h}{1-h'}.\frac{K_w^3}{K'^3_w}.\frac{h'^3}{h^3}.$$

Taking K_w at $100° = 48 \times 10^{-14}$, at $85° = 27.6 \times 10^{-14}$, and at $25° = 1 \times 10^{-14}$, as extrapolated from Noyes' numbers (*Zeitsch. physikal. Chem.*, 1910, **73**, 1), we obtain:

Q between 25° and 100° = 11970 cal.,
Q „ 25° „ 85° = 12860 cal.

Thus the heat of ionisation of one gram-molecule of solid aluminium hydroxide into the ions $Al^{\cdots}$ and OH' is about 12000 cal.

When neutralised by strong acids, one equivalent of aluminium hydroxide should evolve 13·700 calories less than the heat necessary to ionise the molecule, that is,

$$13700 - 4133 = 9567 \text{ cal.}$$

Thomsen found 9320 cal., which agrees with the calculated value, indicating a base of medium strength.

The Diffusion Potential.

Having found the ionic concentrations and the corresponding mobilities, it seemed interesting to compare the potential difference observed on liquid boundaries between single aluminium chloride solutions with the values calculated from Henderson's formula (*Zeitsch. physikal. Chem.*, 1908, **63**, 325). The formula for the diffusion potential E is

$$E = \frac{RT}{F}.\frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')}\log_e\frac{U_1' + V_1'}{U_2' + V_2'},$$

where

$U_1 = u_1c_1 + u_2c_2 + \ldots$ $\qquad V_1 = v_1\bar{c}_1 + v_2\bar{c}_2 + \ldots$

$U_1' = u_1c_1w_1 + u_2c_2w_2 + \ldots$ $\qquad V_1' = v_1\bar{c}_1\bar{w}_1 + v_2\bar{c}_2\bar{w}_2 + \ldots$

c, $\bar{c}$ denoting concentrations of cation and anion,
u, v „ equivalent mobilities of cation and anion,
w, $\bar{w}$ „ valencies of cation and anion respectively.

In the special case of aluminium chloride,

$V_1 = V_1' = M_{Cl} \,.\, cx = 75 \,.\, cx.$
$U_1 + V_1 = K_c$ (specific conductivity), therefore $U_1 = K_c - 75\ cx$.
$U_1 - V_1 = K_c - 150\ cx = c(\lambda_c - 150x)$.

Further, neglecting the hydrolysis,

$$U_1 = c(y_1 M_1 + y_2 \,.\, 2M_2 + y_3 \,.\, 3M_3)$$
$$U_1' = c(y_1 M_1 + 2y_2 \,.\, 2M_2 + 3y_3 \,.\, 3M_3)$$

hence $$U_1' - U_1 = c(2y_2 M_2 + 6y_3 M_3)$$

further $$U_1' + V_1' = c(2y_2 M_2 + 6y_3 M_3) + U_1 + V_1$$
$$= c(\lambda_c + 2y_2 M_3 + 6y_3 M_3).$$

Finally,

$$E = 0{\cdot}059 \frac{c(\lambda_c - 150x) - c'(\lambda_c' - 150x')}{c(\lambda_c + 2y_2 M_2 + 6y_3 M_3) - c'(\lambda_c' + 2y_2' M_2 + 6y_3' M_3)} \times \log \frac{c(\lambda_c + 2y_2 M_2 + 6y_3 M_3)}{c'(\lambda_c' + 2y_2' M_2 + 6y_3' M_3)},$$

TABLE II.

Preliminary Calculations.

Concentration of $AlCl_3$ in equivalent/litre.	λ_c.	x.	y_3.	y_1.	$2M_2y_2 + 6M_3y_3$.	$\lambda_c - 150x$.	$\lambda_c + 2M_2y_2 + 6M_3y_3$.	$a = c(\lambda_c - 150x)$.	$b = c(\lambda_c + 2M_2y_2 + 6M_3y_3)$.
0·1227	85·7	0·730	0·1	0·2	48·4	−23·8	134·1	−2·92	16·45
0·0184	104·7	0·814	0·14	0·18	58·3	−17·4	163·0	−0·32	2·99
0·0092	110·3	0·838	0·16	0·17	63·4	−14·4	173·7	−0·133	1·598
0·00613	113·7	0·851	0·17	0·16	65·3	−14·0	179·0	−0·0858	1·097

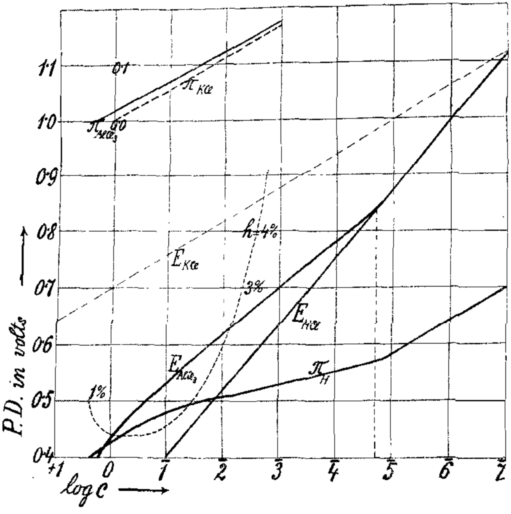
Calculation of $E = 0{\cdot}059 \frac{a - a'}{b - b'} \log_{10} \frac{b}{b'}$ volts.

According to Henderson's paper, the *E.M.F.* is here denoted as positive if the current passes from the first solution to the second inside the cell.

E.M.F. measured between calomel electrodes in $AlCl_3$ solutions of concentration.		*P.D.* of single electrodes.	*E.M.F.* observed without elimination of diffusion *P.D.*	*E* observed.	*E* calculated.
0·1227	0·0184	0·019	0·0100	−0·009	−0·0084
0·1227	0·0092	0·040	0·0290	−0·011	−0·0112
0·1227	0·00613	0·046	0·0321	−0·014	−0·0128
0·0184	0·092	0·017	0·0153	−0·002	−0·0022
0·0184	0·0613	0·027	0·019	−0·008	−0·0032

In table II, the potential differences calculated in this way are compared with those directly observed, this being the first instance in which Henderson's formula could be tested in the case of tervalent ions.

FIG. 2.



The Activity of Hydrochloric Acid in Aluminium Chloride Solutions.

The results of *E.M.F.* measurements are plotted in Fig. 2. The lines marked π_{KCl} and π_{AlCl_3} give the potentials of calomel electrodes in solutions of potassium chloride and aluminium chloride respectively, showing that the activity of chlorine ions in aluminium chloride solutions is very near to that which obtains in equivalent solutions of potassium chloride, the dissociation into chloridions in the case of aluminium chloride being only about 20 per cent. less than in the case of potassium chloride.

The abscissæ in Fig. 2 are in all cases logarithms of the concentration c expressed in gram-equivalents per litre.

The curve $h = \frac{C_{H^{\cdot}}}{c}$ shows the change of hydrolysis with dilution.

The curve π_H represents the potential of the hydrogen electrode in aluminium chloride solutions, referred to the normal calomel electrode as zero (the values to be taken as negative).

The curve E_{AlCl_3} shows the variation of *E.M.F.* of the cell $Hg \mid$ calomel, $AlCl_3$ solution $\mid H_2$, giving the activities of chlorine and hydrogen ions, or the activity of hydrochloric acid, according to the formula

$$E_{AlCl_3} = RT \log_e \frac{P_H \cdot P_{Cl}}{[H^{\cdot}] \cdot [Cl']} = 0{\cdot}2837 - 0{\cdot}0591 \log_{10} [H^{\cdot}] \cdot [Cl']$$
$$= 0{\cdot}2837 - 0{\cdot}1182 \log_{10} [HCl].$$

Thus the curve E_{AlCl_3} shows the partial pressures of hydrochloric acid formed by the hydrolysis of aluminium chloride.

If this curve is compared with the curve E_{HCl}, expressing the partial pressure or activity of pure hydrochloric acid solutions as obtained from the results of Tolman and Ferguson (*loc. cit.*), corrected from 18° to 25°, it is possible to find for every aluminium chloride solution the concentration of pure hydrochloric acid, which would have the same activity of hydrogen chloride (exert the same partial pressure).

Thus in 2·29	N-$AlCl_3$	the HCl tension is that of	0·176	N-HCl.
1·00	,,	,,	,,	0·0582	,,
0·368	,,	,,	,,	0·0184	,,
0·100	,,	,,	,,	0·00617	,,
0·0184	,,	,,	,,	0·00178	,,

the potential difference between calomel and hydrogen electrodes, that is, the ordinate in each pair of solutions being the same.

The values of E_{HCl} for dilute solutions have been obtained by extrapolating from the observed values and assuming that E_H increases by 0·1182 volt for a decrease in concentration of 10 : 1.

Similarly, the line E_{AlCl_3} was produced in the direction corresponding with the theoretical increase of *E.M.F.* by

$$\frac{RT}{F} \log [H^{\cdot}] \cdot [Cl'] = \frac{RT}{F} \log [Al^{\cdot\cdot\cdot}]^{\frac{1}{3}} \cdot c = \frac{RT}{F} \log c^{\frac{4}{3}} = \tfrac{4}{3} \cdot 0{\cdot}0591 \text{ volt}$$

for tenfold dilution, which at the highest dilutions will be greater owing to the decrease of $Al^{\cdot\cdot\cdot}$ ions due to the precipitation as $Al(OH)_3$.

As is seen in the figure, these lines will meet at a normality of

about 0·000027, where practically total hydrolysis is reached, so that in concentrations less than $10^{-5}N$, aluminium chloride behaves similarly to boron trichloride, which is completely hydrolysed in solution; on the other hand, aluminium hydroxide does not dissolve in $10^{-5}N$-hydrochloric acid to form aluminium chloride.

The value of π_H at great dilutions has been assumed to be proportional to $\log[H^{\cdot}]$. From this, the value of π_H in a neutral solution is 0·70 volt.

The line E_{KCl}, representing the activity of hydrochloric acid in solutions of an ideal non-hydrolysable chloride of a strong base, has been drawn, in which π_H is taken as equal to 0·700 volt.

Similar *E.M.F.* curves for chlorides must all lie between the two extremes, namely, E_{KCl} and E_{HCl} lines, the slope becoming steeper as the alkalinity of the metal decreases. Thus a chloride of a strong base like lanthanum trichloride would give a curve very similar to E_{KCl}, whereas boron chloride would give nearly that of E_{HCl}. This would be a precise and distinct way of expressing *hydrolysis.*

Summary.

(1) From conductivity data and *E.M.F.* measurements of aluminium chloride concentration cells, the amount of ionisation and hydrolysis was determined, and the gradual ionisation of cations calculated.

(2) The ionisation of aluminium chloride into chloridions is about 20 per cent. less than the ionisation of potassium chloride of equivalent concentration.

(3) The basic solubility product of aluminium hydroxide is

$$[Al^{\cdot\cdot\cdot}] \cdot [OH']^3 = 1{\cdot}06 \times 10^{-33}.$$

(4) The heat of ionisation of aluminium hydroxide has been calculated.

(5) The mobility of the ion $Al^{\cdot\cdot\cdot} = 3 \times 49{\cdot}2$, that of the ion $AlCl^{\cdot\cdot} = 2 \times 47$.

(6) Henderson's formula for the diffusion potential between solutions of aluminium chloride has been found to hold good.

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IV.—*The Electroaffinity of Aluminium. Part II. The Aluminium Electrode.*

By JAROSLAV HEYROVSKÝ.

Passive Aluminium.

Potentials.—The position of aluminium in the electro-potential series has long remained uncertain. Thus Streinz (*Ber. Wien. Akad.*, 1878, **77**, 410), from measurements in aluminium nitrate solutions, placed aluminium as follows:

$$- \ldots . \text{ Mg, Zn, Cd, Sn, } \frac{\text{Al}}{\text{Pb}}, \text{ Fe} \ldots . +,$$

and from measurements in aluminium chloride solutions thus:

$$- \ldots . \text{ Mg, Zn, Al, Cd} \ldots . +.$$

Wright and Thompson (*Phil. Mag.*, 1885, [v], **19**, 102, 197) found aluminium to be more positive than zinc in solutions of chlorides by 0·280 volt, of bromides by 0·295 volt, and of sulphates by 0·537 volt, although from thermo-chemical determinations they expected a potential one volt more negative than for zinc.

Neumann (*Zeitsch. physikal. Chem.*, 1894, **14**, 193), using amalgamated aluminium, placed it as follows:

$$\ldots \text{ Mg, Al, Mn, Zn} \ldots$$

Burgess and Hambuechen (*Electrochem. Ind.*, 1903, **1**, 165) found that the potential of aluminium wires varied from −0·3 to −1·3 volt (referred to the normal hydrogen electrode).

Van Deventer (*Chem. Weekblad,* 1907, **4**, 625, 771) found that amalgamated aluminium had a potential similar to magnesium, whilst the inactive metal was more noble than zinc.

Obviously, in all cases where the metal is not amalgamated, aluminium remains in a passive condition, the passivity being caused by a skin of oxide or hydroxide, as is evident on dissolving aluminium in dilute alkalis or during amalgamation, when the coherent skin peels off.

The potential of metallic aluminium, like that of any passive electrode, is not influenced by the presence of aluminium ions in solution. The metal behaves rather as a gas electrode, being sensitive to oxidising and reducing agents, besides being influenced by anions (compare Jory and Barnes, *Trans. Amer. Electrochem. Soc.*, 1903, **3**, 95). Great sensitivity to shocks was also observed. The following table of experimental results shows the passivity of aluminium wire:

Cell (at room temperature), first electrode is +.	Behaviour.	Observed *E.M.F.* in volts.
Hg | calomel *N*-KCl soln. | Al	Showing sudden changes and great fluctuations of *E.M.F.*	0·77—1·67
Hg calomel *N*/10-KCl soln. Al	When not moved	0·76—0·80
	Immedately after the aluminium surface has been rubbed on glass fragments.	1·40—1·47
	Allowed to remain.	< 1·0
	Again rubbed.	1·48
	Current of oxygen passed round the electrode.	0·6—0·7 (least observed *E.M.F.*)
	Current of hydrogen passed.	1·38

The potential is most negative in solutions of chlorides; it is less negative in bromides, iodides, sulphates, and most passive in nitrate solutions. Evidently solutions of compounds of a more oxidising character passivify aluminium more intensively. This is in accordance with the known fact (compare Müller, *Zeitsch. physikal. Chem.*, 1909, **69**, 481) that the passivifying influence of an anion is inversely proportional to the solubility of the product formed at the electrode (that is, the oxide).

Dissolution of Metallic Aluminium.—The combined action of the active cation $H^{\cdot}$ and the anions Cl', Br', and I' activates aluminium so that it decomposes water, evolving hydrogen even in the dilute acids. Centnerszwer and Sachs (*Zeitsch. physikal. Chem.*, 1914, **87**, 692) found that the rate of evolution of hydrogen in *N*-hydrochloric acid was 0·066 c.c. per sq. cm. per minute, in *N*-hydrobromic acid 0·002 c.c., and in hydriodic acid still less. The dissolution in *N*-sulphuric acid was much slower, whereas in nitric acid no hydrogen was evolved.

The following experiments were made at the ordinary temperature:

Acid used.	Evolution of hydrogen.	Notes
Sulphuric acid *N*/10.	None.	But solutions in contact with metal for some days were found to contain aluminium salt.
,, *N*.	Slow.	—
,, concentrated.	Slow.	Yellowish or orange coating of sulphur deposits on metal.
Nitric acid, dilute or concentrated.	None.	Solutions were found to contain aluminium salt. If some chloride is added, bubbles are evolved at once.
Hydrochloric acid, dilute or concentrated.	Strong.	If potassium chlorate is added, evolution increases.
Sulphurous acid.	Moderate.	Odour of hydrogen sulphide.

Acid used.	Evolution of hydrogen.	Notes.
Organic acids.	None.	Insoluble.
Potassium iodide and iodine solution.	Slow.	—
Potassium, sodium or barium hydroxides, dilute or concentrated.	Strong.	Concentrated ammonia and potassium carbonate solutions also dissolve the metal.

The dissolution in pure concentrated sulphuric acid is interesting. If we suppose that electrochemical processes cause corrosion, then the precipitation of sulphur on aluminium must be regarded as cathodic deposition, the few cations, S˙˙˙˙˙˙, which might exist in minute quantities in concentrated sulphuric acid being thrown down as a more noble element with less solution tension than aluminium.

Electro-deposition of Metals by Aluminium.—Similarly, the deposition of any other more noble metal on aluminium is influenced by anions present in solution, as they determine the potential of the metallic aluminium.

In this connexion, the following results were obtained:

Solution into which aluminium is dipped.	Deposition of metal.	Evolution of hydrogen.	Notes.
Gold chloride, dilute.	Gold deposits at once.	Strong.	Solution turns violet.
Mercuric chloride, dilute.	Instantly amalgamated.	Strong.	—
Mercurous chloride.	Slow amalgamation.	Slow.	Mercurous chloride must be in contact with metal.
Solution of mercuric oxide in nitric acid.	No action.	—	If trace of chloride is added, amalgamation occurs.
Silver nitrate, dilute or concentrated.	Fine crystals of silver.	None.	—
Cupric chloride, cupric bromide, cupric chloride and potassium iodide.	*Copper deposits readily.*	Slow.	*Solutions decolorise.*
Copper sulphate.	Very slow deposition of copper.	None.	—
Fehling's solution.	,, ,,	Slow.	—
Cupric nitrate.	Scarcely any action.	—.	—
Ammoniacal copper solution.	No action.	—	—
Ferric chloride.	Dark powder deposits.	Slow.	—
Ferrous sulphate.	No action.	—	—
Zinc chloride.	No action.	—	—
Zinc sulphate.	,,	—	—
Alkaline solution of zincate.	Grey crystalline powder.	Slow.	—

Active Aluminium.

Aluminium when active, that is, when dipping into a solution of hydrochloric acid or alkali hydroxide, decomposes water vigorously and cannot be used for precise *E.M.F.* measurements.

Neumann (*loc. cit.*) therefore used amalgamated aluminium, which causes less rapid evolution of hydrogen. He obtained as the mean value of rather variable potentials: in *N*-aluminium sulphate solution $-1\cdot317$ volts, in *N*-aluminium chloride solution $-1\cdot292$ volts, in *N*-aluminium nitrate solution $-1\cdot052$ volts, referred to the normal hydrogen electrode as zero.

Even such an electrode is far from being a reversible one, since the hydrogen ions discharging on the electrode make the potential more positive, just as silver ions do in silver concentration cells. If the evolution of hydrogen could be prevented, that is, if the potential of hydrogen could be lowered below that of aluminium, a reversible aluminium electrode would be obtained.

The potential of amalgamated aluminium wires in $0\cdot0213N$-aluminium chloride solution saturated with hydrogen under atmospheric pressure was, indeed, found to be less variable and more negative, namely, $-1\cdot330\pm0\cdot003$ volts, but slow evolution of hydrogen could not be prevented.

The high overvoltage of hydrogen on a mercury surface makes it possible for a dilute amalgam of a very negative metal to behave as a reversible electrode, because the evolution of hydrogen is almost entirely prevented.

Lewis (*J. Amer. Chem. Soc.*, 1910, **32**, 1458; 1912, **34**, 119; 1913, **35**, 340; 1915, **37**, 1893) has been able to determine the electrolytic potentials of alkali metals using dilute amalgams, and the same method has been adopted here for aluminium.

Preparation of Aluminium Amalgam.—About 0·4 gram of aluminium (99·6 per cent.) was dissolved in 200 grams of pure dry mercury by boiling for two to three hours in an atmosphere of dry carbon dioxide. On cooling, some solid amalgam separated out on the surface, showing that this very dilute (about 0·1 per cent.) amalgam is saturated. This amalgam is extremely easily decomposed in moist air, instantly losing its lustre and becoming covered by hydroxide, this being no doubt due to the great affinity of aluminium for oxygen and its small affinity for mercury.

Whether this saturated amalgam shows any difference of potential from pure active aluminium or not could not be ascertained, since aluminium was found to be passive in dry acetone, ether, or piperidine. However, since the liquid amalgam is in contact with solid amalgam, their solution tensions must be identical, and as

the aluminium seems to be very loosely bound to mercury, the heat of oxidation of the solid amalgam has been found to be the same as the heat of oxidation of aluminium (Baille and Féry, *Ann. Chim. Phys.*, 1889, [vi], **17**, 246). The *electrolytic potential of* the liquid amalgam must be very near to that of ideal active aluminium.

Measurement of E.M.F.—The glass apparatus in which the amalgam had been prepared was inverted, and the amalgam allowed to pass through a side tap, by which the flow could be regulated, into a sealed-on capillary tube (of 1 mm. bore) with a platinum contact. The lower end of the capillary tube was bent up and opened out, so as to provide a larger surface of amalgam. The electrode dipped into a solution of aluminium chloride, which was stirred by means of a stream of hydrogen bubbles. The space above the solution was thus kept filled with hydrogen under atmospheric pressure.

The second electrode was a hydrogen electrode consisting of platinum coated on glass, as used by Loomis and Acree (*Amer. Chem. J.*, 1911, **46**, 585, 621, 638); there was also a calomel electrode attached to the vessel, filled with the same aluminium chloride solution, to check the hydrogen electrode from time to time. The whole apparatus was kept in a thermostat at 25·0°.

At the beginning of each experiment, hydrogen was passed through the cell until the potential difference between the calomel and hydrogen electrode became constant. Then the tap on the capillary tube was opened and the amalgam allowed to drop out slowly. It was found better to allow the amalgam to flow slowly, as on fresh surfaces, after a few seconds, bubbles of hydrogen appeared. Siuce, however, during readings, the potential increased by several millivolts, this being no doubt due to electrical adsorption of ions on drops of mercury, the solution round the electrode was stirred by bubbling hydrogen through it, and simultaneously the aluminium chloride solution, through which hydrogen was first passed, was allowed to flow into the space round the electrode.

A second series of measurements was made with new amalgams aud capillary tubes, and the results obtained did not differ by more than 10 millivolts from the first series, even in the most dilute solutions, whilst in the stronger solutions the agreement was within 3 millivolts.

In this way, the following readings were obtained (using accumulator, Weston cell, Lippmann electrometer, and potentiometer giving readings to 0·1 millivolt):

Concentration of aluminium chlorides in gram-equivalents per litre.	Mean $E.M.F.$ of the cell: $+H_2$ | $AlCl_3$ solution | Al-amalgam.	π_{Al} referred to the normal hydrogen electrode.
(2·88	1·128 volt	−1·284 volt)
0·1845	1·164	−1·370
0·0675	1·160	−1·382
0·0337	1·157	−1·383
0·0213	1·145	−1·381
0·0107	1·161	−1·397
(0·00675	1·135	−1·381)
(0·00213	1·136	−1·377)

The determinations of single hydrogen electrode potentials are described in the preceding paper (p. 15), from which the potentials of aluminium amalgam electrodes, π_{Al} (third column), could be calculated.

The solutions were prepared from aluminium chloride purified by precipitation with hydrogen chloride, and to each solution excess of freshly precipitated aluminium hydroxide was added. In such solutions, the solubility product $[Al^{\cdot\cdot\cdot}] . [OH']^3$ should be constant and equal to $k . [Al(OH)_3]$. Then the electrolytic potential of aluminium becomes

$$E.P. = -\frac{R.T}{3F}\log_e\frac{C_{Al}}{[Al^{\cdot\cdot\cdot}]} = -\frac{R.T}{3F}\log_e\frac{C_{Al}[OH']^3}{k} =$$

$$-\frac{R.T}{F}\log_e\frac{C_{Al}^{\frac{1}{3}}.K_w}{k.[H^{\cdot}]} = -\frac{R.T}{F}\log_e K.[OH'].$$

where K is a constant.

Such an electrode, therefore, behaves as a hydrogen electrode or an oxygen electrode of the type Hg | HgO, and consequently its potential, π_{Al}, should always differ from the platinised electrode by a constant.

The difference between the two electrodes (column 2) is very nearly constant, except in the case of the first solution, which was very viscous and opaque. In the two most dilute solutions the $E.M.F.$'s were rather variable, sometimes approaching 1·16 volts. The value of π_{Al} on the whole falls with the increase of acidity and concentration of aluminium chloride.

In order to determine how the potential of the aluminium electrode is influenced by different solutions, a simpler form of apparatus was used, having two capillary amalgam electrodes dipping into solutions saturated with hydrogen and covered by a layer of liquid paraffin. In this case, the amalgam was not allowed to drop continuously, but the surface was renewed every few minutes.

The values obtained in this way (at 25°) are given in table I. Single potentials are referred to the normal hydrogen electrode.

TABLE I.

Solution used in the Al-electrode.	Second electrode.	Observed *E.M.F.* in volts.	Potential of Al-electrode, π_{Al}.	π_H potential of a hydrogen electrode, dipping in the solution used.	*P.D.* between the Al and H_2 electrode, when both in the same solution $= \pi_H - \pi_{Al}$.	Concentration of hydrions of the solution used.
N/10-HCl	*N*/10-KCl calomel.	1·5790	—1·209	—0·057	1·152	10^{-1}
2·90 *N*-$AlCl_3$	*N*-KCl calomel.	1·54—1·55	1·26—1·27	—0·110	1·15—1·16	8.10^{-3}
0·368 ,,	Calo[illegible]l of the same solution.	1·674	1·374	0·181	1·193	10^{-3}
0·0675 ,,	[illegible]	1·699	1·359	0·202	1·157	4.10^{-4}
0·0409 ,,	,,	1·702	1·342	0·208	1·134	3.10^{-4}
0·0184 ,,	,,	1·724	1·343	0·214	1·129	2.10^{-4}
0·0046 ,,	,,	1·755	1·349	0·230	1·119	$1·4.10^{-4}$
0·00306 ,,	,,	1·770	1·345	0·233	1·112	$1·1.10^{-4}$
0·0028 ,,	*N*-KCl calomel.	1·630	1·347	0·237	1·110	10^{-4}
0·30 *N*-$Al_2(SO_4)_3$	,,	1·700	1·417	—	—	—
0·030 ,,	,,	1·742	1·459	—	—	—
N/10-KCl	,,	1·785	1·502	0·415	1·087	10^{-7}
N-KCl	,,	1·750	1·467	0·415	1·052	10^{-7}
N/100-KOH+$Al(OH)_3$	Hg+HgO of the same solution.	1·910	1·622	0·628	0·994	10^{-11}
N/10- ,, ,,	,,	1·774	1·576	0·718	0·858	10^{-12}
N/10-KOH	,,	1·752	1·613	0·777	0·836	10^{-12}
N-KOH saturated with $Al(OH)_3$	,,	1·713	1·596	0·799	0·797	10^{-13}

Some determinations of single electrode potentials, π_{Al} and π_{H}, are calculated from the results described in the preceding paper; the electrode potentials in potassium hydroxide solutions were obtained by elimination of the diffusion potential with concentrated potassium chloride solutions.

With fresh surfaces, the *E.M.F.* rose a few millivolts to a maximum, and after three minutes began to fall slowly. If the solution round the electrode was stirred or the electrode shaken, the *E.M.F.* fell about 20 millivolts, but reverted to the original value on keeping. Oxidising agents, such as dilute solutions of ferric chloride or hydrogen peroxide, or even a current of air, caused a considerable decrease of negative potential, amounting to several decivolts; reducing agents had no influence.

The more acidic the solution, the more stable was the *E.M.F.* and fewer bubbles of hydrogen appeared on the surface of the amalgam. In *N*/10-hydrochloric acid no bubbles were formed, and the *E.M.F.* was constant for ten minutes at 1·5788 volts, whereas in alkaline solutions there was a visible evolution of minute bubbles.

Discussion of Results.

From the most trustworthy measurements of π_{Al} in

0·1845*N*-$AlCl_3$	$= -1·370$ volts,	where $[Al^{\cdots}]$	$= 0·0130$*
0·0675 ,,	$= -1·382$,,	,,	$= 0·0080$
0·0337 ,,	$= -1·383$,,	,,	$= 0·0044$

the theoretical value for the electrolytic potential of aluminium in a normal solution of aluminium ions *E.P.* has been calculated by the formula

$$E.P. = \pi_{Al} - \frac{RT}{3F}\log_e [Al^{\cdots}] = \pi_{Al} - \frac{0·0591}{3}\log_{10}[Al^{\cdots}].$$

The values $-1·333$, $-1·341$, $-1·336$ calculated in this way give $E.P. = -1·337$ volts as the most probable value.

The approximate value of the electrode potential can be obtained from the heat of the electro-chemical reaction if we neglect the term $T.\frac{d\pi}{dT}$ in the equation $\pi = Q + T.\frac{d\pi}{dT}$ and assume that the heat equivalent, *Q*, of the reaction is equal to the total change of energy.

The heat of the reaction

$$\tfrac{1}{3}Al + HCl \text{ (in 200 aq.)} \longrightarrow \tfrac{1}{3}AlCl_3 + \tfrac{1}{2}H_2$$

* See Part I.

is 41·033 calories (Thomsen). It can be regarded as the difference of heats of ionisation of the processes:

$$\tfrac{1}{3}Al \longrightarrow \tfrac{1}{3}Al^{\cdots} + \ominus$$
$$H \longrightarrow H^{+} + \ominus$$

giving
$$\tfrac{1}{3}Al + H^{\cdot} \longrightarrow \tfrac{1}{3}Al^{+++} + H,$$

from which the calculated potential of the process

$$Al \longrightarrow Al^{\cdots} + 3\ominus$$

is 1·76 volts, whereas the potential corresponding with 31·000 calories of the reaction

$$\tfrac{1}{3}Al + H_2O \longrightarrow \tfrac{1}{3}Al(OH)_3 + \tfrac{1}{2}H_2$$

leads to 1·34 volts. This would apply to the electrochemical process

$$Al + 3OH' \longrightarrow Al(OH)_3 + 3\ominus.$$

The coincidence of the latter value with the observed one was pointed out by Kistiakovsky (*Zeitsch. physikal. Chem.*, 1910, **70**, 260), who suggested similar electrode reactions for magnesium, iron, and chromium.

The reason why only the process

$$Al + 3OH' \longrightarrow Al(OH)_3 + 3\ominus$$

is the source of electrical energy must be sought in the extremely small solubility product of aluminium hydroxide ($=10^{-33}$; see Part I) effecting considerable hydrolysis. Owing to this, the layer of solution close to the surface of the amalgam is saturated with aluminium hydroxide, so that the potential is determined by hydroxyl ion concentration directly, by aluminium ion concentration only through the solubility product equilibrium. This is evident from table I, where with decreasing acidity π_{Al} increases. Owing, however, to increasing oxidation of the amalgam in less acidic solutions, the values are shifted towards more positive potentials, so that in these solutions the potential density from the hydrogen electrode (column 4, table I) decreases instead of being constant.

The reason why even in acidic solutions (like 0·1*N*-hydrochloric acid) the ordinary ionisation potential of $Al \longrightarrow Al^{\cdots} + 3\ominus$ is not attained, but the value remains, roughly, that of

$$Al + 3OH' \longrightarrow Al(OH) + 3\ominus,$$

must be sought in the extremely slight dissociation of aluminium hydroxide, which does not react sufficiently quickly with the acid to form aluminium ions, and remains far behind the reaction

determining the *electrode potential*. Moreover, the second rea tion might be a molecular one, not ionic, thus:

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3aq.,$$

and need not take place at the electrode.

Summary.

(1) Various potentials of passive aluminium have been measure and the influence of the anion on potential, dissolution, a deposition of metals is discussed.

(2) The potential of active aluminium in the form of saturat liquid amalgam has been measured in different solutions.

(3) The theoretical value of $E.P. = -1{\cdot}337$ volts at 25°, t normal hydrogen electrode being taken as zero. The correspon ing electrochemical reaction being

$$Al + 3OH' \longrightarrow Al(OH)_3 + 3\ominus.$$

In conclusion, I desire to express my thanks to Prof. F. (Donnan, at whose suggestion this work was undertaken, for h kind interest and advice. I also wish to express my indebtedne to Dr. R. E. Slade for his constant help throughout th investigation.

CHEMICAL DEPARTMENT,
UNIVERSITY COLLEGE, LONDON. [*Received, October 20th*, 1919.]

V.—*The Propagation of Flame in Mixtures* (*Methane and Air. Part I. Horizont Propagation.*

By WALTER MASON and RICHARD VERNON WHEELER.

IN previous communications to this Society a study of the initi "uniform movement" of flame in gaseous mixtures has been pr sented (T., 1917, **111**, 267, 1044; 1919, **115**, 578). The majori of the experiments of which an account has been given have bee with methane as the combustible gas. The general conclusio drawn as to the character and rationale of the uniform moveme are, however, applicable to all inflammable mixtures.

The uniform movement is one phase in the propagation of flam and is of comparatively short duration. The speeds attained by th

flames during its regime are comparatively slow; very slow compared with that of the detonation-wave, but slow also compared with the speeds during other phases in the propagation of flame in mixtures wherein the detonation-wave normally does not develop.

The value of determinations of the speeds of flames during the uniform movement lies in the measure thereby afforded of the general behaviour of a given inflammable mixture or range of mixtures immediately after ignition, the measurements, when made under standard conditions, being physical constants. Knowledge is, however, often necessary of the maximum speed attainable at any time during the course of the propagation of flame in mixtures of a given combustible gas with air or oxygen. Such knowledge is of prime importance, for example, in respect of mixtures of methane and air, in connexion with the safe working of coal mines.

In the present paper a description is given of the phases, other than the uniform movement, during the horizontal propagation of flame in mixtures of methane and air.

The several series of experiments were carried out in tubes of different dimensions and materials. It is important when comparing one series of experiments with another that due regard should be paid to the details given respecting the tubes employed. In the majority of the experiments measurements of speeds were made by the "screen-wire" method, of which full details have been given in earlier papers (T., 1914, **105**, 2610; 1917, **111**, 1053). Supplementary information was obtained by photographic analysis of the flames. In order to obtain the photographs the flames were caused to travel along a tube of brass, 5 cm. in diameter, furnished with a window of quartz which was focussed on a rapidly revolving film by means of a quartz lens. The use of quartz enabled the light falling on the film to be sufficiently actinic to record the movements of the flames with considerable detail.

(I) *Ignition at the Open End of a Tube Closed at the Other End.*

The initial phase of propagation of flame when the mixture is contained in a horizontal tube closed at one end and open at the other, and ignition is at the open end, constitutes the "uniform movement."

The linear duration of the uniform movement is controlled by the speed of the flame (and thus by the composition of the inflammable mixture); by the length, diameter, and uniformity of bore of the tube; in short, by such factors as influence the establishment of resonance in the column of gases in the tube. Eventually, as a direct outcome of the establishment of resonance, the flame-front

acquires a periodic undulatory motion (see T., 1919, **115**, 584) leading sooner or later to violent vibrations which vary considerably in amplitude but remain periodic.

This phase in the propagation of flame was discovered by Schloesing and de Mondésir, and was termed "le mouvement vibratoire" by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 331). Although accurate record can be obtained of the development of the "vibratory movement" under chosen conditions, the measurements—of the mean speed of the flame, for example—are not of much theoretical significance or practical value, for the speed of the flame during any one vibration, and the amplitude of the vibrations, is very susceptible of changes, designed or inadvertent, in the experimental conditions.

So far as mixtures of methane and air are concerned, it is perhaps sufficient to record a few of the data obtained as indicative of the general character of this phase in the propagation of flame for comparison with the uniform movement which precedes it. Thus, with mixtures containing between 10 and 10·5 per cent. of methane, and with a tube of brass 240 cm. long and 5 cm. in diameter, the significant measurements, obtained by photographic means, are as follow:

Speed of flame during uniform movement ...	*90 cm. per second.*
Linear duration of uniform movement	80 cm.

Faint undulations of the flame-front appear after the flame has travelled 32 cm. The mean speed of the flame is not affected by these undulations; their amplitude is small, and their period is that of the resonating column of gases in the tube. The amplitude of the undulations increases gradually from 1·7 cm. over the distance 32—50 cm. to 1·9 cm. over the distance 50—60 cm. and 2·2 cm. over the distance 60—80 cm. It then begins to increase rapidly, becoming 3·6 over the distance 80—90 cm. During this period of rapid increase in amplitude of the undulations the mean speed of the flame falls to 64 cm. per second. Eventually, the "vibratory movement," which owes its origin to an undulation of abnormal amplitude, is established.

During the vibratory movement the oscillations of the flame are of wide amplitude—25 cm. or more—and the mean speed of translation of flame is considerably enhanced. It will be seen on examination of Plate I, Fig. 1, that the change of speed from that of the uniform movement (90 cm. per sec.) to that of the vibratory movement (278 cm. per sec.) is fairly abrupt, and that the latter speed is maintained at a constant mean value over a considerable distance. Finally, as the flame approaches the closed end of the tube,

its mean speed decreases, although it still continues to vibrate to the end.

In the table that follows, data are given respecting successive portions of the vibratory movement, each portion being specified by the distance along the tube over which the flame travelled.

Vibratory Movement of Flame.

(Tube of brass 240 cm. long and 5 cm. in diameter. Methane 10—10·5 per cent. in air.)

Distance along tube.	Mean speed of flame. Cm. per sec.	Maximum speed during forward motion of flame. Cm. per sec.	Amplitude of vibrations. Cm.	Frequency of vibrations. Mean values.
0—80 cm.	—	Uniform movement	—	—
80—90	64	292	3·6	47·7
90—107	—	Gradual change	—	—
107—170	278	2,430	26·0	70·0
170—200	—	Gradual change	—	—
200—220	62	416	1·4	45·0
220—240	38	—	—	—

It may be noted that, as indicated by the frequency of the vibrations, the resonating column of gases is that lying between the closed end of the tube and the flame-front at any given moment. Thus the calculated mean value for the frequency of vibration of a column of gases in an unflanged tube of brass 5 cm. in diameter is 48 if the tube is 130—140 cm. long and 74·5 if it is 50—93 cm. long.

These measurements bear reference only to the particular conditions of experiment specified, but they could be reproduced with an exactness which must be considered remarkable when the complicated character of the phenomena is borne in mind. In this respect better fortune has attended the experiments than that which befel Mallard and Le Chatelier, who have stated: "En repétant plusieurs fois la même experience dans des conditions identiques à elles-mêmes, le mouvement vibratoire ne se reproduit jamais deux fois de la même façon" (*loc. cit.*, p. 333). No doubt the rapid speed of flame in the mixture ($CS_2 + 6NO$) employed by Mallard and Le Chatelier for their experiments would tend to emphasise irregularities in the results.

It has already been stated that the vibratory movement is the direct result of the resonance of the column of gases in the tube. It was shown, in connexion with experiments on the propagation of flame in mixtures of acetylene and air, that resonance, by whatever means induced, can be made manifest by the undulatory motion of flame as it travels along tubes, the periods of the undulations agreeing closely with the periods calculated for organ-pipes of the dimen-

sions of the tubes employed. As the resonance becomes stronger, the amplitude of the undulations of the flame front perforce increases, since the flame acquires its motion from the vibrating column of gases. There is thus produced an agitation of the gaseous mixture which eventually becomes of sufficient importance to affect appreciably the speed of a flame travelling through it. (In this connexion, see T., 1919, **115**, 81.)

The vibratory movement is, indeed, an excellent example of the effect of agitation or turbulence in accelerating the translation of flame through a gaseous mixture. The effect is a mechanical one. During each forward impulse the flame is drawn rapidly through previously unburnt mixture by reason of the motion acquired by the resonating column of gases. In a certain degree, also, the forward motion of the flame is assisted by the expansion in volume of the burning gases, especially when the flame is at some distance from the open end of the tube, so that escape of the expanded gases there is retarded. The latter effect is more pronounced when the mixture is ignited at the closed end of a tube open at the other end, conditions which will be considered in the succeeding section of this paper.

(II) *Ignition at the Closed End of a Tube Open at the Other End.*

The two phases in the propagation of flame, the "uniform movement" and the "vibratory movement," are characteristic of what occurs with mixtures of a combustible gas and air when ignition is at the open end of a tube closed at the other end. Under such conditions, with some combustible gases (for example, hydrogen) when mixed with air, and with all when mixed with pure oxygen, the vibratory movement is succeeded by the detonation-wave, provided that the combustible gas and oxygen are in suitable proportions.

With no mixture of methane and air (at atmospheric temperature and pressure) is the detonation-wave thus developed, but the vibratory movement continues until the flame is extinguished, either on reaching the closed end of the tube or, occasionally, during an abnormally extensive backward movement, before the end is reached.

When ignition of a mixture of methane and air is at the closed end of a tube open at the other, no uniform movement takes place, but the speed of the flame increases rapidly as it travels towards the open end.

For comparison with the uniform and vibratory movements, experiments were made with a series of mixtures in a horizontal tube of glass 5 cm. in diameter and 500 cm. long. Fine screen-

wires of copper were stretched across the tube at half-metre distances, and the times taken for the flames to travel between these screen-wires measured by the method described in previous communications. The mixtures were ignited at a spark-gap 3 cm. from the closed end.

The speed of the flame in some of the mixtures reached 29 m. per second over the last half-metre length of the tube, and, so far as could be judged, was nearly uniformly accelerated from the beginning. It seemed possible, therefore, that with a tube of greater length and larger diameter a permanent maximum velocity of flame, such as is characteristic of the detonation-wave, might eventually be attained.

A steel tube 30·5 cm. in diameter and 90 m. long was used to test this supposition. It was found that flame did not continue to propagate in any mixture beyond a distance of 15 m. from the closed end, at which ignition was effected. Violent vibrations were developed after the flame had travelled 10 m., in the course of which the flame was extinguished. The same result was obtained when the mixtures were ignited *a few cm.* (ten to twenty) from, instead of at, the closed end, a condition which would have the effect of imparting an impetus to the flame at the beginning, thereby hastening the development of the detonation-wave (compare Dixon, *Phil. Trans.*, 1903, A., **200**, 345).

The extinction of the flame after travelling such a short distance in a long tube under the conditions of these experiments is no doubt caused by the products of combustion, when cooling, tending to produce a partial vacuum behind the flame (the end of the tube from which the flame started being sealed), which is therefore dragged back over part of the path it has already travelled. This may occur several times, the flame alternately leaping forward and being drawn back, but eventually a sufficient proportion of the burnt mingles with the unburnt gases to prevent further propagation of flame.

(III) *Ignition at One End of a Tube open at Both Ends.*

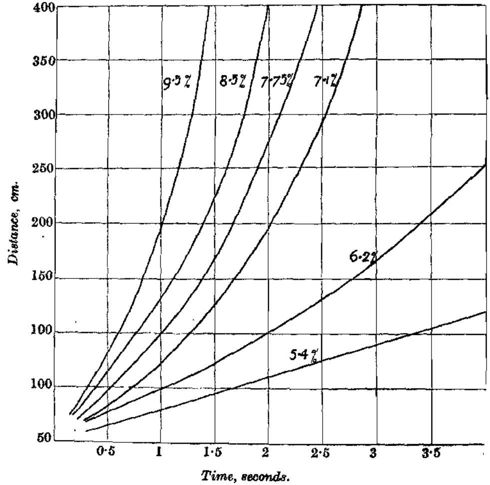
If the reason assigned for the extinction of the flame when travelling from the closed to the open end of a long tube is correct—a reason intended to apply only to such comparatively slowly-moving flames as are obtained with mixtures of methane and air *—extinc-

* With mixtures of coal-gas and air, for example, in which the flames are initially more rapid than with methane and air, the vibratory movement continues (in a steel tube 30·5 cm. in diameter) until the detonation-wave is developed. The speed of the wave, in a mixture containing 17 per cent. of coal-gas, is 1750 m. per second.

tion should not occur when both ends are open (so that the cooling of the products of combustion cannot create a partial vacuum behind the flame), and the speed at which the flame travels should be rapid.

Several series of experiments were made to test this point, it being important to determine the conditions under which the most rapidly moving flames are obtained in mixtures of methane and air, and the order of magnitude of the speeds.

FIG. 1.



The first series of experiments was in a tube of glass 5 cm. diameter and 500 cm. long, for comparison with the series, carri out in the same tube, in which ignition was at a closed end. T results are shown graphically in Fig. 1, in which distance along t tube is plotted against time, zero time being the moment of fusi of the first screen-wire, which was 10 cm. from the point of igniti

With all but the lower-limit mixture (5·40 per cent. methan in which the speed of flame is uniform, there is a gradual and,

far as the records can indicate, regular acceleration of speed as the flame travels from end to end of the tube. In no instance did extinction of the flame occur, although in most of the experiments slight vibrations were noticed at different stages in the development of the propagation, the incidence of these vibrations being earlier the more rapid was the flame. There was, also, with the mixtures richer in methane, a noticeable check in the progress of the flame as it approached a particular point, succeeded by a spurt forward after that point had been passed. This effect seemed traceable to a slight ridge around one of the small holes with which the tube had been pierced (by means of a blow-pipe flame) to receive the screen-wires used to record the time of passage of the flame. This ridge projected less than 1·5 mm. within the tube; the fact that it could markedly affect the progress of a flame in a tube 50 mm. in diameter is a striking example of the sensitiveness of flames to turbulence in the mixture, even such slight turbulence as the small projecting ridge would cause. This subject will be dealt with in a subsequent communication.

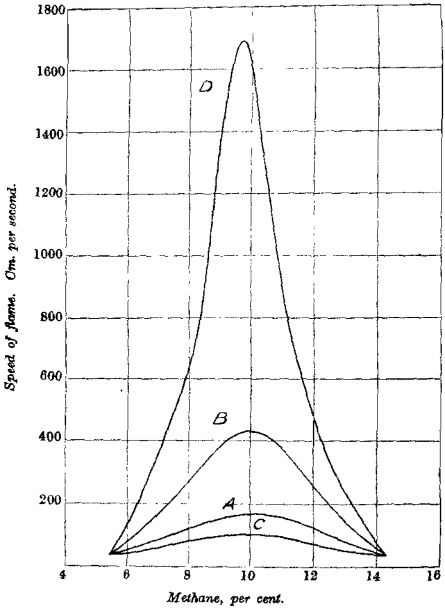
Another series of experiments covered the whole range of inflammable mixtures of methane and air, and was made in a glass tube 9 cm. in diameter and 620 cm. long. This series is of value for comparison of the mean speeds of the flame over measured distances with the speeds of the uniform movement in a tube of the same diameter. Such a comparison is made diagrammatically in Fig. 2, which records speed-percentage curves (A) for the distance (measured from the point of ignition) 50—100 cm., and (B) for the distance 407—467 cm. in the tube open at both ends, the speeds being the mean speeds of the flames over those distances; and (C) for the uniform movement. In addition, a curve (D) is given showing the mean speed of flame over the distance 20—120 cm. in a tube 5 cm. in diameter closed at one end and open at the other, ignition being at the closed end.

The mean speed over the distance 407—467 is seen to be greatest in the mixture containing 10 per cent. of methane, and to be about four times the speed of the uniform movement in that mixture in a tube of the same diameter. The speed of the flame in all mixtures (except the limit mixtures) was found, as with the tube of 5 cm. in diameter, to increase continuously over the whole distance travelled, and, as when ignition was at the closed end of a similar tube, it seemed possible that the detonation-wave might be developed if the flame could travel far enough. If not, it was necessary to know what change in the character of the propagation would interpose to prevent it.

The steel tube, 30·5 cm. in diameter, was brought into requisition

to test this. The length of the tube in the first instance was 15·25 m., and records were obtained of the times taken for the flame to travel measured distances from the point of ignition in different mixtures. *As usual, the fastest speed* of flame was obtained with mixtures containing between 9·5 and 10·5 per cent.

Fig. 2.



of methane, but no speed approaching that of the detonation-wa was recorded, the maximum being 917 cm. per second, attain after travelling 14 m. in a mixture containing 10·25 per cent. methane.

It appeared from the records that the flame, which could not

directly observed, had acquired a vibratory character after travelling half the length of the tube. No indication of this was given by the sound of the flames as they travelled, and the vibrations were presumably of small amplitude. Vibratory propagation in the steel tube, such as was obtained when one end of the tube was closed, had hitherto been accompanied by a staccato note, but the flames now produced seemed, to the ear, to travel unhaltingly from one end of the tube to the other, issuing into the air with a sharp report.

The length of the tube was therefore increased to 90 m. in the expectation that, if the flame had indeed become vibratory in character after travelling 6 or 7 m., a greatly increased distance of travel would produce readily recognisable vibrations of large amplitude. Such was, in fact, the result; the propagation ultimately became strongly vibratory, but the early stages of the propagation were profoundly modified by the increased length given to the tube. Instead of increasing rapidly in speed from the beginning, as when the tube was 15·25 m. in length, the flames now travelled from the point of ignition at a constant and comparatively slow speed over a distance of between 12 and 15 m. (dependent on the composition of the mixture) and then began to vibrate. The vibrations acquired their greatest amplitude about half-way along the tube and continued throughout the remaining distance.

In mixtures containing between 9·5 and 10·5 per cent. of methane the speed of the flame over the first 12—15 m. averaged 200 cm. per second. Thus, the records obtained over this range of mixtures were:

Methane, per cent.	Initial speed of flame. Cm. per second.
9·60	198
9·70	188
9·75	203
10·10	213

This speed is a little faster than that of the uniform movement in similar mixtures in the same tube (170 cm. per second). The important point is, however, that the speed should remain constant over so great a distance. Although open at both ends, a long tube is thus found to impress upon a flame started at one end conditions similar to those obtaining with a shorter tube closed at the distal end. The resistance to the expansive force of the burning gases afforded by the long column of unburnt mixture in advance of the flame corresponds (nearly) in effect with the resistance of a closed end; so close is the correspondence that the flame is caused to proceed at the outset with a "uniform movement," but little faster

than the uniform movement as ordinarily developed in mixtures of the same methane-content in a tube of the same diameter.

Photographic Analysis of the Flames.

In Plate 1 are shown time-distance curves, obtained photographically, for the propagation of flame in a 10 per cent. mixture of methane and air in a tube of brass 5 cm. in diameter and 240 cm. long.

The flames travelled horizontally from right to left, and the photographic film can be regarded as moving vertically upwards, its speed of travel being 30 cm. per second. The full length of the tube, 240 cm., is shown in the photographs, each of which is composite, being obtained by joining together photographs of successive sections of the tube 30 cm. in length.

For Fig. 1 the tube was closed at the left-hand end, and ignition was at the right-hand, open, end; for Fig. 2 the tube was open at both ends, and ignition was at the right-hand end; and for Fig. 3 the right-hand end of the tube was closed, and ignition was effected there, the left-hand end being open.

The relative speeds at which the flame traversed the full length of the tube are readily deduced from these photographs, which also illustrate the general behaviour of the flames under the different conditions of ignition of the mixtures, and require no description. It should be noted, however, that Fig. 3 discloses the presence of rapid vibrations during the progress of the flame which, as stated earlier in this paper, was judged by visual observation to travel unchecked through the tube at a speed which, according to determinations by the screen-wire method, seemed to be nearly uniformly accelerated.

In Plates 2 and 3 details of the flames as they passed through a section of the tube 30 cm. in length are shown, the section chosen being that indicated in Plate 1 by the vertical white lines. To obtain these photographs the speed of the film was increased to 90 cm. per second. Calculations made from them are as follow:

PLATE 2.

Tube closed at one end; ignition at open end.

Mean speed of flame	245 cm. per sec.
Maximum speed during forward movement of vibration	1,990 cm. per sec.
Average frequency of vibrations ...	76

The calculated frequency for the fundamental tone of the tube during the longitudinal vibration of air within it is 68 if the length

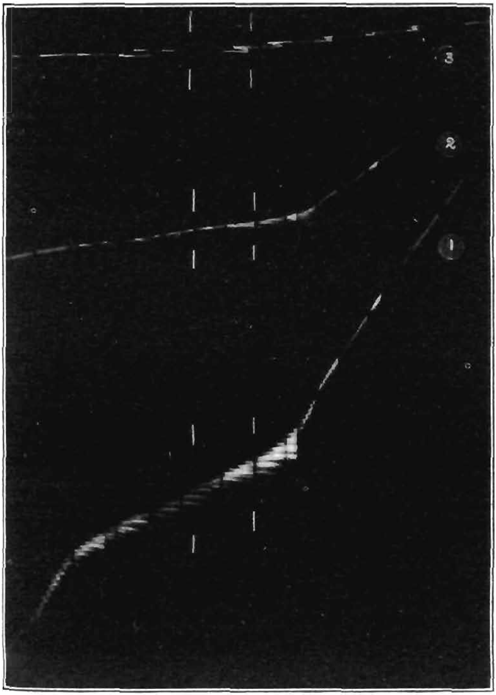


PLATE 1.

[To face p. 46.

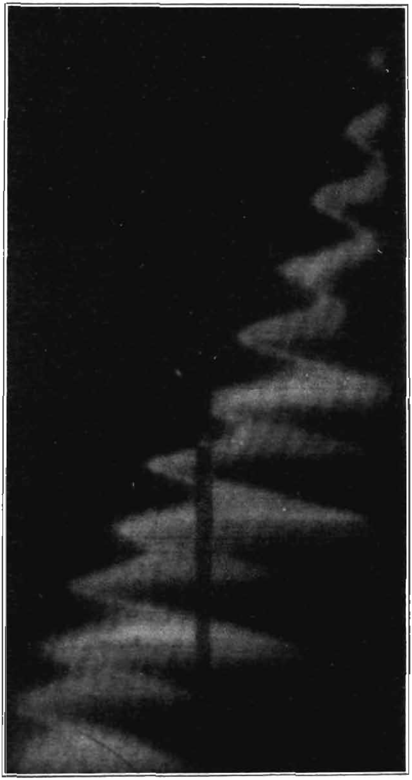


PLATE 2.

Fig. 1.

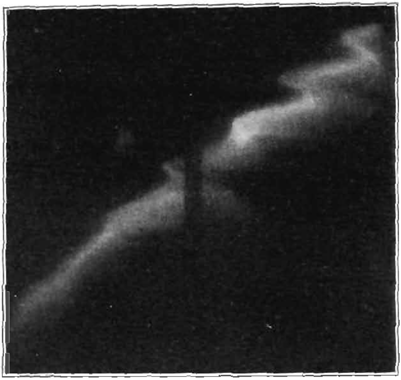


Fig. 2.

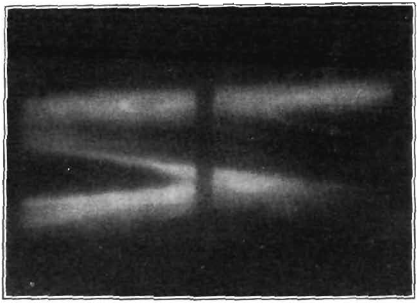


Plate 3.

of the vibrating column be assumed to be 125 cm. and 88 if 95 cm. These are the distances of the flame-front from the closed end of the tube at the beginning and end of the photograph respectively. The mean value is 78.

PLATE 3, FIG. 1.

Tube open at both ends; ignition at one end.

Mean speed of flame	480 cm. per sec.
Maximum speed during forward movement of vibration	3,730 cm. per sec.

PLATE 3, FIG. 2.

Tube closed at one end; ignition at closed end.

Mean speed of flame	1,050 cm. per sec.
Maximum speed during forward movement of vibration	5,760 cm. per sec.
Amplitude of vibrations	30 cm.

Of the three conditions under which the ignition of mixtures of methane and air has been effected in these experiments, that which would lead to the most disastrous results in industry is the third—ignition at one end of a tube or gallery open at both ends. For although the initial speed of the flame is not then so great as when ignition is at a closed end, continued propagation is assured, and there may be developed momentarily during the vibratory motion velocities and pressures as great as any produced throughout the life of a flame started at a closed end.

The fastest speed of flame recorded in any experiment was about 60 m. per second, and was of short duration. This is not of the same order of magnitude as the speed of the detonation-wave in gaseous mixtures. It would not be wise to conclude, however, that the detonation-wave cannot, in any circumstances, be developed in mixtures of methane and air at normal temperature and pressure. On the contrary, in several experiments in the steel tube, 90 m. long and open at both ends, in which restrictions were introduced at two points (consisting of steel rings which reduced the diameter of the tube to 28·6 cm. at those points), the development of the detonation-wave seemed imminent. Further description of these experiments, which are being continued, is reserved until the subject of the effects of turbulence on the propagation of flame in gaseous mixtures is discussed.

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VI.—*The Propagation of Flame in Complex Gaseous Mixtures. Part IV. The Uniform Movement of Flame in Mixtures of Methane, Oxygen, and Nitrogen. "Maximum-speed Mixtures" of Methane and Hydrogen in Air.*

By WILLIAM PAYMAN.

IT is customary to describe the inflammation of a gas mixture containing hydrogen and oxygen, for example, as the "burning of hydrogen in oxygen." This phrase is purely a relative one, it being, of course, equally correct to regard the combustion as the burning of oxygen in hydrogen. Thus the upper limit of inflammability of hydrogen in oxygen is the lower limit of inflammability of oxygen in hydrogen.

Mixtures of a combustible gas with air can be considered in a similar way. If, however, we state that the combustible gas, hydrogen, for example, is burning in air, the alternative expression would be that the oxygen is burning in a mixture of nitrogen and hydrogen. A comparison can, in fact, be made over a range of inflammable mixtures, between hydrogen and air on the one hand, and, on the other, mixtures of oxygen with a mixture (or "atmosphere") containing nitrogen and hydrogen in constant proportions.

For all practical purposes, atmospheric air may be regarded as a mixture of oxygen and nitrogen in constant proportions. To investigate thoroughly the mode of combustion of complex inflammable gas mixtures, it is evidently desirable to examine their behaviour with "atmospheres" other than air, the simplest problem being no doubt the combustion of a pure, inflammable gas, such as methane, in pure oxygen.

The uniform movement during the propagation of flame in mixtures of methane with different atmospheres containing less oxygen than air has been examined by Mason and Wheeler (T., 1917, **111**, 1044). The present research deals with mixtures containing more oxygen than air, and with mixtures with pure oxygen. The detonation-wave in such mixtures has been studied by Dixon (*Phil. Trans.*, 1893, **184**, 97). The speed of propagation of flame by detonation is of a different order from that during the initial, uniform movement of flame, which is supposed to be mainly effected by the conduction of heat from the burning to the adjacent unburnt

layer of gas mixture. The speed of the detonation-wave is, however, uniform. The two modes of propagation of flame, "uniform movement" and "detonation-wave," may be compared with respect to mixtures of hydrogen and air. The speed of the detonation-wave in the mixture of air with hydrogen containing the correct proportions for complete combustion is 1930 metres per second in a tube 9 mm. in diameter (value extrapolated from those determined by Dixon, *loc. cit.*), whilst the speed of the uniform movement of flame in the same mixture (in a horizontal glass tube 2·5 cm. in diameter) is 4·8 metres per second (Haward and Otagawa, T., 1916, **109**, 83).

Maximum-speed Mixtures.—If we neglect losses of heat to the walls of the containing vessel, the speed of propagation of flame during the uniform movement can be regarded as depending mainly on two factors, namely, (1) the rate of conduction of heat from layer to layer of the mixture, which in turn depends on the difference in temperature of the burning and the unburnt gases and on their thermal conductivities, and (2) the rate of reaction of the combining gases, which for a given combustible gas will vary with the composition of the mixtures (presumably according to the usual laws of mass action) and with the temperature produced by the reaction. A third factor might be added, namely, the ignition-temperature of the mixtures, but this is perhaps dependent on the other factors.

The mixture of hydrogen and air for complete combustion, that is to say, the mixture having the greatest heat of combustion, contains 29·6 per cent. of hydrogen, but the mixture in which the speed of the uniform movement of flame is greatest contains about 38 per cent., or nearly 10 per cent. in excess. This fact is usually explained by reference to the high thermal conductivity of hydrogen, which is $31 \cdot 9 \times 10^{-5}$, as compared with $5 \cdot 22 \times 10^{-5}$ for air. A similar displacement of the maximum-speed mixtures is, however, observed with all inflammable gases when mixed with air, including (as was shown in Part III of this series of papers) gases, such as carbon monoxide, the thermal conductivities of which are less than that of air.*

Consider the effect of mass action when methane burns in a given atmosphere of nitrogen and oxygen. Let this atmosphere contain a per cent. of oxygen. According to the law of mass action, the rate of reaction will be proportional to $C_{CH_4} \times C^2_{O_2}$. Let the mixture in which the rate has its maximum value contain x per cent. of methane.

* The value for the thermal conductivity of carbon monoxide is $4 \cdot 99 \times 10^{-5}$.

Then

$$C_{CH_4} \times C^2_{O_2} = (x) \times \left[(100 - x)\frac{a}{100}\right]^2$$
$$= x(100 - x)^2\left(\frac{a}{100}\right)^2.$$

Since a is constant, the term into which it enters will be at a maximum when $x(100-x)^2$ is at a maximum. That is to say, provided it remains constant, *the composition of the atmosphere* does not affect the methane content required to give the expression $C_{CH_4} \times C^2_{O_2}$ *its maximum* value. It can be shown that this expression reaches a maximum when x, the percentage of methane, is 33·3. Similarly, with hydrogen and any atmosphere of oxygen and nitrogen of constant proportion, the factor representing the effect of mass action is at a maximum when the mixture contains 66·7 per cent. of hydrogen.

In every instance with a given atmosphere, when this remains unaltered, *the maximum effect of the mass-action factor is theoretically* attainable with mixtures containing more combustible gas than is required for complete combustion (except with an atmosphere of pure oxygen, when the mixture for complete combustion is also, theoretically, that for the maximum effect of mass action).

The rate of chemical reaction increases rapidly with rise of temperature. In a series of mixtures of a combustible gas with an atmosphere of constant composition, the highest calorific effect is produced by the mixture containing combustible gas and oxygen in combining proportions. This factor will therefore act in an opposite sense to mass action and will diminish the "displacement" of the maximum-speed mixture caused by the latter factor. For this reason the amount of displacement will be influenced by the cooling effect of excess of combustible gas, and the higher the specific heat of this excess gas at the temperature of reaction the less will be the displacement.*

When *oxygen burns in an* "atmosphere" of constant composition, composed of nitrogen and a combustible gas, the displacement of the maximum mixture should take place towards mixtures containing excess of oxygen. This can be tested experimentally. Just as the whole series of inflammable mixtures of methane and air can be obtained by starting with the mixture containing the reacting gases in combining proportions, and adding either methane or air to it, in the same way a series of mixtures of oxygen with an "atmosphere" of nitrogen and methane can be obtained, by *adding excess of oxygen* or excess of "atmosphere" to the

* This consideration accounts for the wider "displacement" obtained with carbon monoxide than with hydrogen when mixed with air.

mixture of methane and air in combining proportions, which may be termed the "basic mixture." This procedure has the advantage of enabling a direct comparison to be made between methane–air and oxygen–"atmosphere" mixtures, the two series having a common point.

The results of two such series of determination of the speed of the uniform movement of flame in mixtures of oxygen with (i) an atmosphere of nitrogen and methane, and (ii) one of nitrogen and hydrogen, are given in table I. The determinations were carried out in a horizontal glass tube 1·5 metres long and 2·5 cm. in diameter.

TABLE I.

Speed of Uniform Movement of Flame in Mixtures of Oxygen with Mixtures of Constant Composition ("Atmospheres") of Nitrogen and a Combustible Gas.

Methane as the combustible gas.			Hydrogen as the combustible gas.		
Basic mixture : 9·5 per cent. CH_4; 19·0 per cent. O_2; 71·5 per cent. N_2.			*Basic mixture* : 29·6 per cent. H_2; 14·8 per cent. O_2; 55·6 per cent. N_2.		
Methane. Per cent.	Oxygen. Per cent.	Speed. Cm. per sec.	Hydrogen. Per cent.	Oxygen. Per cent.	Speed. Cm. per sec.
6·67	43·3	35·0	16·06	53·7	171
7·51	46·2	61·9	21·76	37·3	488
8·29	39·5	84·3	25·72	25·9	660
8·75	25·6	97·3	29·60	14·8	410
9·07	22·9	91·4	30·50	12·2	234
9·18	22·0	85·4			
9·50	19·0	66·7			
9·67	17·8	37·5			

It will be seen that the displacement of the maximum-speed mixture in both series of experiments, as anticipated, is towards mixtures containing an excess of oxygen. In table II the displacements are compared with those found with the combustible gases burning in air.

TABLE II.

Displacement of Maximum-speed Mixtures.

	Methane.		Hydrogen.	
	O_2–N_2 constant. Methane. Per cent.	CH_4–N_2 constant. Oxygen. Per cent.	O_2–N_2 constant. Hydrogen. Per cent.	H_2–N_2 constant. Oxygen. Per cent.
Mixture for maximum speed of uniform movement of flame	9·9	24·8	38·5	23·4
Mixture in combining proportions. (Basic mixture)	9·5	19·0	29·6	14·8
Displacement	0·4	5·8	8·9	8·6

The addition of either combustible gas or oxygen to the basic mixture results in an increase in speed of the flame. According to the laws of mass action, it would he expected that the displacement would be greater on the addition of oxygen than on the addition of methane (since one molecule of methane combines with two molecules of oxygen for complete combustion); this is found to be so. The displacement should be less with oxygen than with hydrogen (since two molecules of hydrogen combine with one molecule of oxygen); experiment again shows this deduction to be correct. The fact that the specific heat of oxygen is lower thau that of methane and much lower than that of hydrogen, however, would have the effect of decreasing proportionally the amount of displacement caused by excess of either of the two last-named gases. Thus the *displacement caused by the addition of oxygen is found to be much* greater than that caused by methane, but only a little less than that caused by hydrogen.*

The Uniform Movement of Flame in Mixtures of Methane, Oxygen, and Nitrogen.

The speeds of the uniform movement of flame in mixtures of methane with atmospheres containing 13·7, 21, 33, 50, 66, and 100 per cent. of oxygen have been determined. The experiments were carried out in a horizontal glass tube, 2·5 cm. in diameter, as used for earlier experiments. A comparatively short tube, 1·5 metres in length, was used in order to avoid the development of the detonation-wave. With the fastest speeds of flames, however, the detonation-wave was developed after the flame had travelled less than a metre, so that for some of the experiments it was necessary to replace the last metre of the glass tube by a piece of lead piping of the same length and internal diameter.

Only the slowest speeds, up to about 300 cm. per second, were determined by means of the automatic commutator and single recording stylus usually employed for such work in this laboratory; for faster speeds recourse was had to delicate Deprez indicators with separate styli for each screen-wire recording on a smoked paper chart fixed to a rapidly revolving drum. The fastest speeds in mixtures of methane with pure oxygen were determined photographically by the method described by Mason and Wheeler (T., 1919, **115**, 578). A comparison between the two last-named methods of recording speeds of flames gave closely agreeing results.

The results of the determinations are given in table III, and

* These experiments explain why the displacement of the maximum-speed mixture was found to be so small with the mixtures of producer gas and air, as described in Part III.

TABLE III.

Speed of Uniform Movement of Flame in Mixtures of Methane with Different Atmospheres of Nitrogen and Oxygen in a Horizontal Glass Tube 2·5 cm. in Diameter.

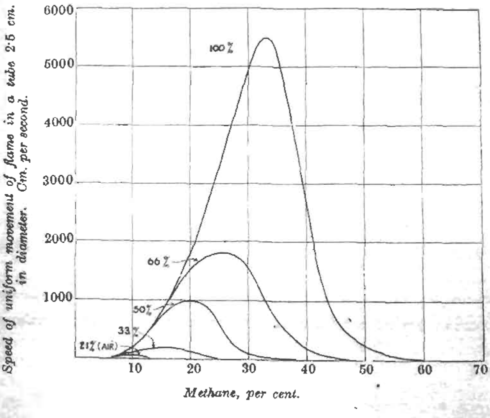
Atmosphere. 13·7 per cent. O_2.		Atmosphere. 33 per cent. O_2.		Atmosphere. 50 per cent. O_2.		Atmosphere. 66 per cent. O_2.		Atmosphere. 100 per cent. O_2.	
Per cent. CH_4.	Speed (cm. per sec.).	Per cent. CH_4.	Speed (cm. per sec.).	Per cent. CH_4.	Speed (cm. per sec.).	Per cent. CH_4.	Speed (cm. per sec.).	Per cent. CH_4.	Speed (cm. per sec.).
6·33	Flame about 15 cm.	5·69	Flame about 10 cm.	5·70	Flame about 15 cm.	5·70	Flame about 15 cm.	5·59	Flame about 5 cm.
6·41*	21·9	5·78	23·0	5·83	22·8	5·84	21·3	5·72	19·9
6·70	21·0	5·87	23·9	9·60	150	8·79	96·5	10·52	266
6·90	19·1	8·44	97·6	12·48	401	11·75	430	15·53	722
7·02	Flame about 6 cm.	11·01	168	15·38	735	15·07	861	21·63	2300
		14·58*	232	19·84*	967	18·41	1307	26·95	3991
		18·01	200	24·01	711	25·08*	1822	33·00*	5502
		21·51	49·1	28·47	171	29·29	1660	36·14	3940
		25·12	18·9	33·58	44	34·65	576	40·00	3020
		25·41	Flame about 15 cm.	38·78	18·9	40·02	155·4	45·61	488
				39·26	Flame about 15 cm.	46·93	20·8	53·36	82·3
						47·50	19·4	57·67	28·8
						47·63	Flame about 4 cm.	59·23	18·9
								59·50	Flame about 30 cm.

diagrammatically in Fig. 1. For the values for mixtures with air, reference should be made to the table in Part II (T., 1919, 115, 1448). The mixture marked with an asterisk in each column is that which contains methane and oxygen in combining proportions.

Fig. 1 may be compared, so far as its general characteristics are concerned, with the similar diagram given by Mason and Wheeler (*loc. cit.*, p. 1048) for mixtures of methane with atmospheres containing less oxygen than air. It should, however, be noted that these authors determined the speeds in a tube 5 cm. in diameter.

The most striking results are those for mixtures of methane with

FIG. 1.



pure oxygen. It will be seen that the maximum speed of the uniform movement of flame is obtained, as was anticipated, with the mixture containing methane and oxygen in combining proportions ($CH_4 + 2O_2$). This result is in sharp distinction from what obtains when the detonation-wave is developed in mixtures of methane and oxygen, for the mixture in which the speed of the detonation-wave is greatest contains equal proportions of methane and oxygen. The difference is the more striking when it is remembered that the uniform movement gives place to the detonation-wave after quite a short distance of travel of the flame.

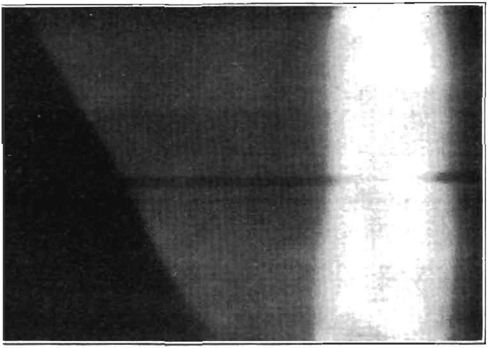


FIG. 3.

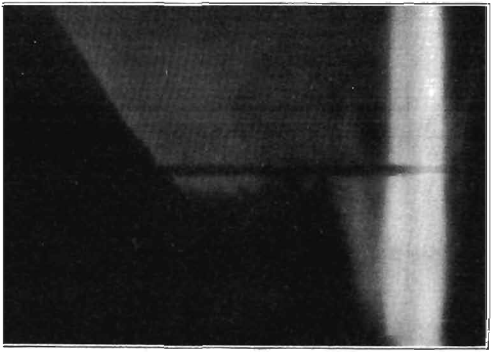


FIG. 2.

[To face p. 54.

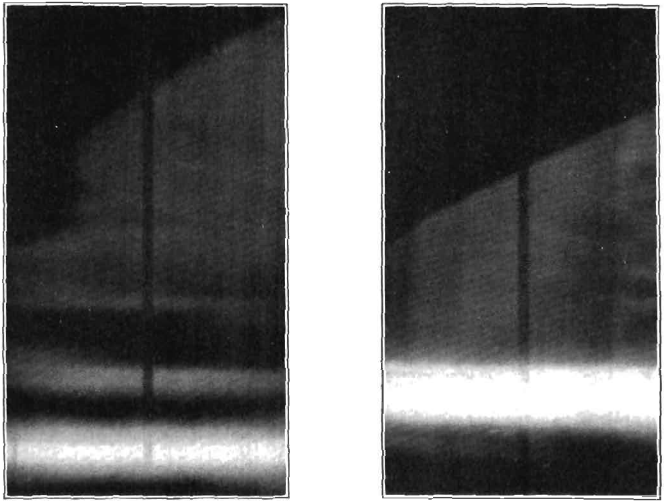


Fig. 5.

In table IV a comparison is made between the speed of the uniform movement and that of the detonation-wave in the five mixtures used by Dixon (*loc. cit.*, p. 181).

TABLE IV.

Comparison of the Speeds of the Detonation-wave and the Uniform Movement in Mixtures of Methane and Oxygen.

Composition of mixture.	Speed, metres per second.	
	Detonation wave. Tube 0·9 cm. diam.	Uniform movement. Tube 2·5 cm. diam.
$2CH_4+8O_2$	1963	18
$2CH_4+6O_2$	2146	33
$2CH_4+4O_2$	2322	55
$2CH_4+3O_2$	2470	25
$2CH_4+2O_2$	2528	2

The addition of methane to the mixture for complete combustion (CH_4+2O_2) is thus seen to increase the speed of the detonation-wave, but markedly to decrease the speed of the uniform movement of flame.

This effect is well illustrated by photographs of the flames (1) in a mixture containing just sufficient oxygen for complete combustion of the methane, and (2) in a mixture containing rather more methane (40 per cent.). In the latter mixture (Fig. 2), the uniform movement persisted over about 25 cm. of travel of the flame, which then vibrated rapidly for a short time (0·06 sec.) without moving further along the tube. The vibrations were followed by a rapid acceleration of the flame, resulting in the detonation-wave, which shattered the glass tube at about 25 cm. distance from the lead extension piece. The bright band at the bottom of the photograph is caused by the "retonation-wave."*

Although the speed of the uniform movement of flame is slower in a mixture containing 40 per cent. of methane than in one containing 33 per cent., the detonation-wave is developed sooner in the former. With the 33 per cent. mixture, the uniform movement extends across the whole width of the photograph (Fig. 3). The incidence of the detonation-wave a short distance further along the tube (within the lead extension piece) is indicated by the bright band due to the retonation-wave, at the bottom of the photograph.†

* A compression-wave sent back, simultaneously with the development of the detonation-wave, through the burnt or still burning mixture (Dixon, *Phil. Trans.*, 1902, **200**, 315).

† The length of tube photographed was 30 cm., and the speeds of the film were 592 and 752 cm. per second for Fig. 2 and Fig. 3 respectively.

It must be admitted that the displacement of the maximum-speed mixture away from that required for complete combustion is not very great in mixtures of methane and air. A better test of the soundness of the conclusion that with pure oxygen the *maximum-speed mixture and the complete-combustion mixture* should coincide should be obtained with a combustible gas like hydrogen. With this gas, it will be remembered, the maximum-speed mixture with air is displaced by as much as 10 per cent. Experiments were therefore made with mixtures of hydrogen and pure oxygen.

Three mixtures were examined, and the speeds are recorded in table V, with the speeds of the detonation-wave in the same mixture for comparison.

TABLE V.

Comparison of the Speeds of the Detonation-wave and the Uniform Movement in Mixtures of Hydrogen and Oxygen.

	Speed, metres per sec.	
Hydrogen. Per cent.	Detonation-wave. Tube 0·9 cm. diam. (Dixon).	Uniform movement. Tube 2·5 cm. diam.
59·9	2650	5·74
66·6	2824	6·62
75·2	3140	5·15

Fig. 4 and Fig. 5 are the photographs of the flames in the mixtures containing 75·2 per cent. and 66·6 per cent. of hydrogen respectively.* It will be seen that the photographs are similar in general character to those obtained with the two corresponding mixtures of methane and oxygen.

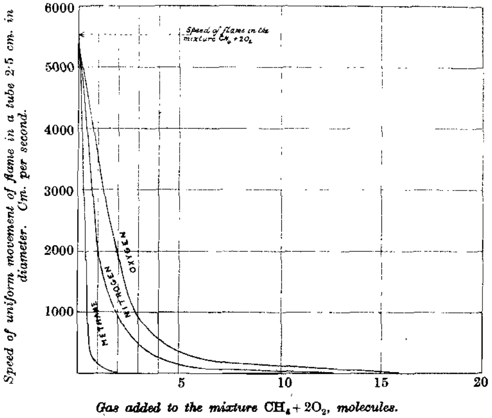
To revert to the experiments with methane, the addition of either methane or oxygen, like that of the inert gas, nitrogen, to the mixture of methane with pure oxygen of the composition $CH_4 + 2O_2$, results in a reduction of the speed of the uniform movement of flame. The relative effects of these three gases are shown in Fig. 6. Methane, having the highest specific heat of the three, has the greatest retarding effect. Although oxygen and nitrogen have approximately the same specific heat, the retarding effect of the former is appreciably less, owing to the effect of mass action when the gas added is capable of taking part in the reaction.

The application of the "speed generalisation" was shown in earlier papers to be restricted by the fact that the only data avail-

* The speeds of the films were 784 and 816 cm. per second for Fig. 4 and Fig. 5 respectively.

able for use in the calculations were those respecting mixtures of inflammable gases with air. Thus with methane–hydrogen–air mixtures no calculations could be made for mixtures in which the speed of flame was greater than 67 cm. per second, the maximum speed in mixtures of methane and air. The speeds now obtained in mixtures of methane with atmospheres containing more oxygen than air are often greater than the maximum speed with hydrogen–air mixtures, so that the use of these values should render it

Fig. 6.



possible to calculate the speeds of the uniform movement of flame in any methane–hydrogen–air mixture.

For this purpose, however, it would be necessary to determine the speed of flame in mixtures of hydrogen with different atmospheres in the same way as has been done for methane, and for similar calculations to be made for mixtures of an industrial gas with air, similar determinations would be required for each individual gas present in the industrial gas.

Such a series of determinations is outside the scope of the present work. It is, however, important to establish the fact that the "speed generalisation" is capable of extension in this manner.

To this end, a few determinations have been made for methane–hydrogen–air mixtures.

To simplify the calculations, mixtures of methane and hydrogen with just sufficient air for complete combustion were chosen. A curve similar to the one in Fig. 6 for $CH_4+2O_2+xN_2$ was constructed for hydrogen ($2H_2+O_2+xN_2$). If mixtures are selected from these two curves in which the speed of flame is the same and is intermediate between the maximum speeds in methane–air and hydrogen–air mixtures, it is possible to mix them in such proportions that the resulting mixtures will contain nitrogen and oxygen in the ratio in which they are found in air. This mixture will have the same speed of uniform movement of flame, will contain combustible gas and oxygen in combining proportions, and will be, in a sense, a methane–hydrogen–air mixture. In this way, it is possible to determine the speed of flame in all mixtures of methane and hydrogen with sufficient air for their complete combustion. The results of such calculations with three simple mixtures are recorded in table VI.

TABLE VI.

Speed of Uniform Movement of Flame.

Hydrogen–Methane mixture.	Cm. per sec.		
		Calculated.	
	Found.	*From curves.*	*From formula.*
H_2+3CH_4	85	90	95
H_2+CH_4	135	140	149
$3H_2+CH_4$	240	250	246

The results recorded in the last column are obtained by use of a formula similar to the one used in Part II (T., 1919, **115**, 1452) for calculating the maximum-speeds of flame in mixtures with air, "mixture for complete combustion" being substituted for "maximum-speed" mixture.

The experimental work described in this series of papers was carried out at the Home Office Experimental Station under the general direction of Dr. R. V. Wheeler.

ESKMEALS,
CUMBERLAND.

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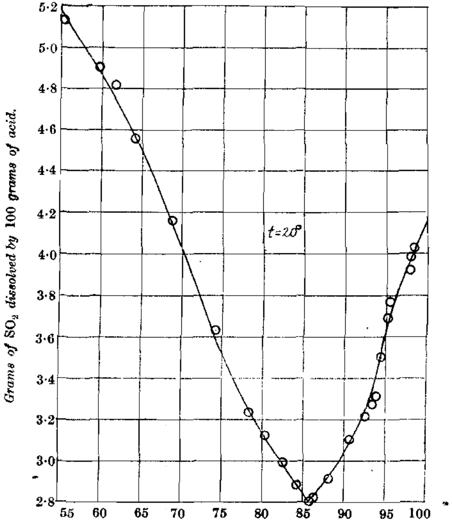
VII.—*The Solubility of Sulphur Dioxide in Sulphuric Acid.*

By FRANK DOUGLAS MILES and JOSEPH FENTON.

IN the course of some work on the gas-purifying system of a plant for the manufacture of sulphuric acid by the "contact" process it was noticed that 95 per cent. sulphuric acid dissolved more sulphur



Percentage of H_2SO_4 *in acid.*

dioxide than did acid of 85 per cent. The solubility in more dilute acid diminishes in the usual manner as the concentration increases, so that the observation pointed to some peculiarity in the solubility curve for higher concentrations of acid. A determination of the

curve was therefore undertaken in the region most technically important, namely, with acid from 50 to 100 per cent., at 20°.

No sufficiently detailed measurements of this kind appear to have been made, although the coefficients of solubility have been given by Kolb for acid varying from 10 to 81 per cent. (*Bull. Soc. Ind. Mulhouse*, 1872, 222). The coefficients of solubility in acid of D 1·84, from 0° to 90°, have also been determined by Dunn (*Chem. News*, 1882, **45**, 282).

To obtain rapid saturation of sulphuric acid, especially when the acid is concentrated, and therefore viscous, is by no means easy. It was found most satisfactory to use small amounts—15—20 grams—in thin test-tubes placed in a thermostat. The acid was stirred vigorously by means of a mechanical stirrer, while a stream of sulphur dioxide was passed in so that the mixture was churned into a froth exposing a very large surface to the gas. Precautions were taken to prevent admission of air to the tube, and to maintain the temperature at 20°±0·1.

Samples were obtained by rapidly drawing the saturated mixture, by means of slight suction, into small weighed glass bulbs, each holding about a gram and made by drawing out glass tubing, so that rather wide capillary ends remained. After sealing and weighing quickly, these bulbs were dropped, two for each analysis, into (1) *N*-sodium hydroxide in slight excess, (2) *N*/10-iodine in slight excess, mixed with 100 c.c. of water. The bulbs were broken and the titrations carried out as usual. Experiment showed that the concentrated sulphuric acid had no influence on the iodometric test.

Analyses were made in each experiment until the results were nearly constant. Generally, the acid-content tended to rise slightly on account of the drying action of the gas. The results are given below. The temperature was 20°, and a correction was applied when the barometer diverged appreciably from 760 mm.

Sulphuric acid. Per cent.	Sulphur dioxide dissolved by 100 grams of acid. Grams.	Sulphuric acid. Per cent.	Sulphur dioxide dissolved by 100 grams of acid. Grams.
55·1	5·13	88·1	2·9
59·6	4·90	90·8	3·10
61·6	4·82	92·8	3·21
68·9	4·16	93·7	3·27
74·1	3·63	94·0	3·31
78·3	3·23	94·6	3·50
80·2	3·12	95·5	3·69
82·5	2·99	95·6	3·77
84·2	2·88	96·5	3·83
85·3	2·83	98·0	3·98
85·8	2·80	98·5	4·03
86·5	2·82	—	—

These figures are shown graphically in the accompanying curve.

The solubility reaches a minimum value in sulphuric acid of 86·0 per cent., and from that point the curve inclines very sharply upward for either increase or decrease in percentage of sulphuric acid. It is significant that acid of 84·5 per cent. has the composition of the hydrate, H_2SO_4,H_2O, and that in the neighbourhood of this point the temperature of melting, and other physical properties, pass through critical values.

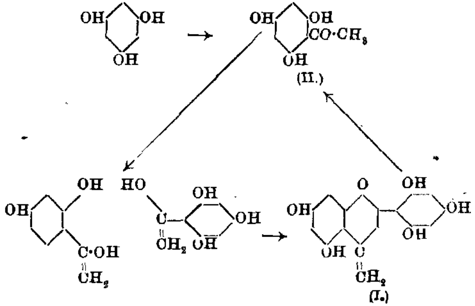
[*Received, December 18th*. 1919.]

VIII.—*Phloroacetophenone.*

By Kiemud Behari Sen and Praphulla Chandra Ghosh.

Phloroacetophenone is an important compound for the synthesis of many natural dyes (Goschke and Tambor, *Ber.*, 1912, **45**, 1237). Bülow and Wagner obtained it by first condensing phloroglucinol with benzoyl chloride and then degrading the resulting pyranol (*Ber.*, 1901, **34**, 1798). Leuchs and Sperling (*Ber.*, 1915, **48**, 135) prepared it by the action of water at 170° on Jerdan's lactones (T., 1897, **71**, 1111). In no case was the direct synthesis achieved.

Resacetophenone, gallacetophenone, and similar compounds are easily and directly prepared from the corresponding phenols by heating them with acetic acid and zinc chloride. It was therefore thought that phloroglucinol on similar treatment might give phloroacetophenone, and thus a direct synthesis might be effected. When, however, phloroglucinol is heated with acetic acid and zinc chloride there is produced a yellow, crystalline compound dissolving in potass-



ium hydroxide solution with a pink colour and fluorescence. From the analysis and the determination of the molecular weight by the ebullioscopic method in alcohol it is concluded that phloroacetophenone is first formed, but that two molecules at once combine, giving a pyran derivative resembling Nencki's resacetein (p. 61).

On boiling the pyran derivative (I) with 10 per cent. sodium hydroxide solution the heterocyclic ring is broken and phloroacetophenone (II) is obtained.

The melting point of phloroacetophenone was found to be 284—285°; according to Bülow and Wagner, it does not melt up to 280°, and Leuchs and Sperling give 218°. The substance obtained by the latter authors contained one molecule of water of crystallisation, which may account for the difference in melting point.

EXPERIMENTAL.

5 : 7-*Dihydroxy*-2-o-o-p-*trihydroxyphenyl*-4-*methylene*-1 : 4-*benzopyran* (I).

Two grams of phloroglucinol were dissolved in 2 c.c. of glacial acetic acid, 3 grams of zinc chloride added, and the whole was gently boiled for ten to fifteen minutes. The yellow liquid was dissolved in hot hydrochloric acid and the clear solution, on cooling, deposited yellow needles (0·9 gram). The substance is soluble in alcohol, and dissolves in potassium hydroxide solution, giving a pink, fluorescent solution. It does not melt up to 290°:

0·1256 gave 0·2751 CO_2 and 0·0502 H_2O. C=59·7; H=4·45.*

0·5713, in 18 c.c. alcohol, gave E=0·18°. M.W.=275.

$C_{16}H_{12}O_6,H_2O$ requires C=60·3; H=4·4 per cent. M.W.=300.

Acetyl Derivative.—One gram of the above compound, 10 c.c. of acetic anhydride, and a few drops of pyridine were boiled gently for an hour. The semi-solid mass obtained on pouring into water was dissolved in acetic acid and precipitated with water, being finally crystallised from dilute acetic acid. The compound melts at 80° and begins to decompose at about 90°:

0·1202 gave 0·2680 CO_2 and 0·0560 H_2O. C=60·8; H=5·1.

$C_{26}H_{22}O_{11}$ requires C=61·16; H=4·31 per cent.

Phloroacetophenone (II).

Three grams of the pyran were dissolved in 75 c.c. of 10 per cent. sodium hydroxide solution, the solution boiled for ten to twelve minutes, and, after cooling, acidified with dilute hydrochloric acid. The precipitate was collected, dried, and finally crystallised from a

mixture of alcohol and dilute hydrochloric acid. The product (0·8 gram) was almost colourless, and dissolved in potassium hydroxide solution with only a pale yellow colour. It melted at 284—285°. (Found, C=56·44; H=5·2. $C_8H_8O_4$ requires C=57·1; H=4·8 per cent.)

Phenylhydrazone.—This was prepared in the ordinary way by dissolving the phloroacetophenone in a mixture of alcohol and acetic acid, adding a little more than the theoretical quantity of phenylhydrazine hydrochloride and sodium acetate, and warming for a few minutes. To the clear solution water was added, and the precipitate was collected, dried, and finally crystallised from dilute alcohol. It decomposes at 237—240°:

0·1150 gave 11·65 c.c. N_2 at 32° and 761 mm. N=11·3.
$C_{14}H_{14}O_3N_2$ requires N=10·8 per cent.

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IX.—*The Peroxides of Bismuth.*

By RICHARD ROBERT LE GEYT WORSLEY and PHILIP WILFRED ROBERTSON.

THE most comprehensive and recent work on the peroxides of bismuth is by Gutbier and Bünz (*Zeitsch. anorg. Chem.*, 1906, **48**, 163, 295; **49**, 433; **50**, 211). These observers, from their experiments on the oxidation of bismuth hydroxide in the presence of alkali hydroxide, drew the conclusion that chemical compounds could not be isolated from the mixtures thus obtained, even after subsequent treatment with nitric acid. It seemed, however, probable that continuous grinding with dilute nitric or glacial acetic acid might bring about a separation of the lower oxide of bismuth from the peroxide. Accordingly, preliminary experiments were carried out in which (*a*) bismuth hydroxide precipitated in the oxidising medium, and (*b*) ordinary bismuth trioxide, were treated with ammonium persulphate in boiling dilute sodium hydroxide solution. The first product was comparatively rich in bismuth peroxide, but its composition altered only little after grinding with glacial acetic acid; the product in the second case contained less peroxide, but, after several grindings, its composition approximated to that of bismuth tetroxide. Experiments were therefore made

in this manner with different oxidising agents in the presence of sodium or potassium hydroxide of different concentrations. In dilute solutions, bismuth tetroxide was the only product; in more concentrated solutions, higher oxides were also formed. These products were analysed in the following manner: the peroxidic oxygen was estimated (*a*) by distillation with hydrochloric acid (Bunsen's method), (*b*) when the substance was soluble, by dissolving in hot nitric acid (D 1·2) and measuring the liberated oxygen; the peroxidic oxygen plus water was determined by heating to redness. The compounds for which analytical results are given below were free from sodium or potassium.

Action of Chlorine on Bismuth Trioxide suspended in Boiling Alkali Hydroxide.

The duration of each experiment was about half an hour. The product of the reaction in dilute solution (5—10 per cent.) was either Bi_2O_4 (brown) or Bi_2O_4,H_2O (brown). The exact conditions determining the formation of the anhydrous oxide or the hydrate could not be ascertained. In concentrated alkali hydroxide (35—40 per cent.) there was formed a mixture of Bi_2O_5,H_2O (red) and $Bi_2O_4,2H_2O$ (yellow), from which the lower oxide could be fractionally separated by the action of hot nitric acid (D 1·4). The following values were obtained in one typical experiment for a mixture: (*A*) after two grindings with glacial acetic acid; (*B*) after three grindings with glacial acetic acid; (*C*) after one extraction with hot nitric acid; (*D*) after two extractions with hot nitric acid:

	A.	*B*.	*C*.	*D*.
Peroxidic-O	5·20	5·05	3·94	3·47
Peroxidic-O + H_2O	10·05	10·02	9·97	10·00

$Bi_2O_4,2H_2O$ requires O = 3·10; O + H_2O = 10·08 per cent.
Bi_2O_5,H_2O requires O = 6·22; O + H_2O = 9·73 per cent.

According to Deichler (*Zeitsch. anorg. Chem.*, 1899, **20**, 111), the product of the reaction should be a mixture of Bi_2O_4 and Bi_2O_5,H_2O, and the $Bi_2O_4,2H_2O$ is produced by the action of nitric acid on the latter. The colour of the substance *A* (orange-red), the analytical results, and its behaviour with nitric acid all indicate that it was a mixture of $Bi_2O_4,2H_2O$ (yellow) and Bi_2O_5,H_2O (red).

Action of Ammonium Persulphate or Potassium Ferricyanide on Bismuth Trioxide suspended in Boiling Alkali Hydroxide.

The product of the reaction in dilute solution was either Bi_2O_4 (brown or purplish-black) or Bi_2O_4,H_2O (brown or purplish-black).

The experimental conditions determining the formation of these four varieties could not be ascertained. In concentrated alkali there was formed, in addition to Bi_2O_4 or Bi_2O_4,H_2O, a small amount of Bi_2O_6 (yellow), which could be fractionally separated from the lower oxide by the action of hot nitric acid (D 1·2).

Bismuth Tetroxide, $Bi_2O_4(BiO_2)$.

This was prepared by the action of chlorine, ammonium persulphate, or potassium ferricyanide on bismuth trioxide suspended in a dilute solution of boiling alkali hydroxide, and the following modifications have been obtained: I, Bi_2O_4 (brown); II, Bi_2O_4 (purplish-black); III, Bi_2O_4,H_2O (brown); IV, Bi_2O_4,H_2O (purplish-black).

The following are typical analyses for preparations which had been ground with glacial acetic acid in an agate mortar until they were completely free from bismuth trioxide and occluded alkali hydroxide:

	I.	II.	Bi_2O_4.
Peroxidic-O	3·31	3·26 ; 3·20* ; 3·39	3·33 per cent.
Loss on heating	3·27	3·24 3·61	3·33 ,,

	III.	IV.	Bi_2O_4,H_2O.
Peroxidic-O	3·25 ; 3·07	3·13 ; 3·21	3·21 per cent.
Peroxidic-O + H_2O.........	6·88 ; 6·20	6·22 ; 6·92	6·83 ,,

* Determined gasometrically.

The brown and purplish-black anhydrous bismuth tetroxides appear to be physical isomerides, and are both stable at 100°. The modifications with one molecule of water lose the water in a vacuum (1 mm.) over phosphoric oxide, slightly darkening in colour. At 100° in the steam-oven, they lose half this amount:

	III.	IV.
Loss at 100°	1·70, 1·74	1·89

Bi_2O_4,H_2O requires $\frac{1}{2}H_2O = 1·81$ per cent.

At 160° all varieties decompose, with the liberation of oxygen.

Bismuth tetroxide is soluble in nitric acid (D 1·2) at 70—90°, yielding its peroxidic oxygen in the gaseous form (with small quantities of ozone). It is peculiarly reactive, immediately oxidising manganous salts in the presence of dilute nitric acid, even in the cold. Bismuth tetroxide is very sparingly soluble in concentrated alkali hydroxide, with the formation of an unstable per-salt.

Another distinct variety, $Bi_2O_4,2H_2O$ (yellow), is formed, together with Bi_2O_5,H_2O, by the action of chlorine on bismuth

trioxide in boiling concentrated alkali hydroxide. It may be fractionally separated from the higher oxide by treatment with boiling nitric acid (D 1·4), in which it is only sparingly soluble. The following analyses were obtained for two preparations:

	I.	II.	$Bi_2O_4,2H_2O$.
Peroxidic-O	3·47	3·38	3·10 per cent.
Peroxidic-O + H_2O......	10·00	9·95	10·08 ,,

At 100° it decomposes, darkening in colour, with the loss of both oxygen and water.

Bismuth Pentoxide, Bi_2O_5.

The monohydrate, Bi_2O_5,H_2O (red or brown), soluble with difficulty in hot concentrated nitric acid, is obtained (*a*) mixed with $Bi_2O_4,2H_2O$ by the action of chlorine on bismuth trioxide in boiling concentrated alkali hydroxide, (*b*) in small quantities mixed with Bi_2O_4,H_2O by the action of ammonium persulphate on bismuth trioxide in dilute alkali hydroxide at 40—60°, when the action is allowed to continue for five to six hours. The bismuth pentoxide produced by the first method could not be separated from the admixed $Bi_2O_4,2H_2O$; obtained according to the second reaction, it could be completely separated from the Bi_2O_4,H_2O by extraction with hot nitric acid (D 1·2). Three different samples gave the following values on analysis:

	I.	II.	III.	Bi_2O_5,H_2O.
Peroxidic-O	5·97	6·05	6·26	6·22 per cent.
Peroxidic-O + H_2O...	9·80	—	10·16	9·73 ,,

A second variety, Bi_2O_5,H_2O (brown), readily soluble in hot nitric acid (D 1·2), is obtained from commercial sodium bismuthate after repeated grinding with glacial acetic acid. The following analyses were obtained for three different preparations:

	I.	II.	III.	Bi_2O_5,H_2O
Peroxidic-O	6·20*	6·19*	6·14	6·22 per cent
Peroxidic-O + H_2O...	10·00	9·91	9·96	9·73 ,,

* Determined gasometrically.

Anhydrous bismuth pentoxide would appear to be incapable of existence. The hydrate, when left in a vacuum (1 mm.) over phosphoric oxide, darkens in colour and slowly loses water and oxygen. At 100° the decomposition is more rapid; in one experiment the percentage of peroxidic oxygen fell from 6·2 to 1·9 in twenty days, and subsequently remained constant, indicating that bismuth trioxide and bismuth tetroxide had been formed in approximately equal amounts.

Bismuth Hexoxide, $Bi_2O_6(BiO_3)$.

Bismuth hexoxide is obtained in small quantities by the action of ammonium persulphate or potassium ferricyanide on bismuth trioxide suspended in boiling concentrated alkali hydroxide, together with bismuth tetroxide (Bi_2O_4 or Bi_2O_4,H_2O), from which it can be separated by continuous extraction with warm nitric acid (D 1·2). It may also be prepared by the oxidation of the tetroxide and subsequent treatment of the product with nitric acid. Bismuth hexoxide is pale brown and contains no water. At the ordinary temperature it loses oxygen slowly, darkening in colour. This would explain the slightly low results obtained on analysis:

	I.	II.	Bi_2O_6.
Peroxidic-O......	8·96	9·13	9·37 per cent.
Loss on heating	9·00	9·11	9·37 „

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X.—*The Action of Mercuric Cyanide on Metallic Salts.*

By LILANANDA GUPTA.

THE action of mercuric cyanide on different metallic salts has been the subject of investigation by previous workers, for example, Poggiale (*Compt. rend.*, 1846, **23**, 762), Varet (*Bull. Soc. chim.*, 1891, [iii], **5**, 8), Bloxam (*Ber.*, 1883, **16**, 2669), etc. In this paper, the action of mercuric cyanide on the chlorides of copper, cobalt, nickel, manganese, cadmium, chromium, vanadium, and aluminium, the nitrates of silver and lead, and ammonium molybdate has been studied. The method of procedure was, however, somewhat different from that adopted by Poggiale and others. A concentrated solution of mercuric cyanide was added to an excess of the salt solutions, and the mixture evaporated slowly on the water-bath. The precipitate which was obtained in each case was collected and washed, as a rule, with the minimum quantity of cold water, and next with alcohol. In the case of the aluminium compound, the concentrated solution was evaporated in a vacuum, and the crystals obtained were washed with alcohol alone.

It is to be noted that the general method of preparing a double cyanide of two metals is to bring together their respective cyanides

or to treat an alkali cyanide with some other double cyanide of the metals in question. The action of mercuric cyanide on the chlorides of copper and cobalt and silver nitrate producing, respectively, the compouuds $CuCN,2Hg(CN)_2,4H_2O$, $Co(CN)_3,Hg(CN)_2,5H_2O$, and $AgCN,Hg(CN)_2,4H_2O$, described in this paper, are thus exceptions to this general rule. On the other hand, Poggiale and Bloxam mention the compounds $2CoCl_2,Hg(CN)_2,4H_2O$ and

$$7AgCN,2HgO,Hg(CN)_2$$

as the products of reaction. Hofmaun and Wagner (*Ber.*, 1908, **41**, 319), however, obtained the salt $AgNO_3,Hg(CN)_2,2H_2O$ in the last case.

Other compouuds described in this paper are $4AlCl_3,HgCl_2,28H_2O$ and $MnCl_2,Hg(CN)_2,2H_2O$. Cryoscopic determinations of the molecular weights in aqueous solutions of these salts have been carried out; also measurements of the conductivity of the latter salt were made at different dilutions.

EXPERIMENTAL.

Compound $CuCN,2Hg(CN)_2,4H_2O$.

About 24 grams of cupric chloride were dissolved in 100 c.c. of water, and a solution of mercuric cyanide containing 10 grams of the salt was added, the final volume of the mixture being 300 c.c. This was evaporated slowly on the water-bath almost to one-third its original bulk, and was set aside. Next morning, a very fine precipitate had formed, which was collected, washed first with cold water, and finally with alcohol, and dried on a porous plate at 25°.

The product had a pale violet colour, shining like fine sand when held in the sunlight, and under the microscope was seen to consist of cubes. It is not appreciably soluble in water, but decomposes and passes into solution when treated with sulphuric acid:

I. 0·2011 gave 0·0258 CuO. Cu = 10·25.
0·2786 ,, 0·1680 Hg. Hg = 60·32.
0·2161 ,, 18·6 c.c. N_2 at 24° and 760 mm. CN = 18·21.
II. 0·2125 ,, 0·0262 CuO. Cu = 9·97.
III. 0·2618 ,, 0·0318 CuO. Cu = 9·70.
0·3242 ,, 0·1960 Hg. Hg = 60·46.
0·2838 ,, 26·2 c.c. N_2 at 32° and 760 mm. CN = 18·39.

$CuCN,2Hg(CN)_2,4H_2O$ requires Cu = 9·47; Hg = 60·15; CN = 19·54 per cent.

Compound $Co(CN)_3,Hg(CN)_2,5H_2O$.

This was prepared by the action of mercuric cyanide on cobalt chloride. The proportions of the salts were as 1 : 3, and the method

of procedure was exactly the same as mentioned above. A visible reaction took place within ten minutes from the start; the colour of the solution deepened, and slow precipitation commenced. The washings and drying were performed as before.

The compound is sparingly soluble in water, but decomposes and passes into solution by the action of sulphuric acid, as is the case with all sparingly soluble cyanides:

0·3118 gave 0·043 Co. Co = 12·79.
0·2440 ,, 0·0977 Hg. Hg = 40·04.
0·1875 ,, 25·46 c.c. N_2 at 26° and 760 mm. CN = 27·78.
$Co(CN)_3,Hg(CN)_2,5H_2O$ requires Co = 12·31; Hg = 41·40; CN = 27·13 per cent.

Nickel Cyanide, $Ni(CN)_2,3H_2O$.

About 20 grams of nickel chloride, $NiCl_2,6H_2O$, were dissolved in 100 c.c. of water, and to the cold solution was added a filtered solution of mercuric cyanide (8 : 100). The details of the procedure were exactly the same as in the foregoing cases.

Williams ("Cyanogen Compounds," p. 65) describes the compound, $Ni(CN)_2,7H_2O$, which he obtained by treating an alkali cyanide with excess of a nickel salt. The compound obtained by the above method is not at all gelatinous, it has a fine, granular structure, and is insoluble in water or dilute acids, but is decomposed by concentrated sulphuric acid. Two preparations gave the same product in each case:

I. 0·3852 gave 0·1751 NiO. Ni = 35·71.
0·2348 ,, 35·4 c.c. N_2 at 0° and 760 mm. CN = 31·61.
II. 0·2605 gave 0·1186 NiO. Ni = 35·78.
0·4348 ,, 0·1408 H_2O. H_2O = 32·38.*
$Ni(CN)_2,3H_2O$ requires Ni = 35·75; CN = 31·51; H_2O = 32·74 per cent.

The estimation of water in this compound and in subsequent determinations was carried out in the following manner.

In a combnstion furnace was placed a hard-glass combustion tube containing a known amount of the substance to be dehydrated in a weighed porcelain boat. One end of this tube was joined successively to a sulphuric acid wash-bottle, a calcium chloride U-tube, a soda-lime tower, a second sulphuric acid wash-bottle, and finally to an air-supply. To the other end, a U-tube containing pumice stone soaked in sulphuric acid was attached. A guard tube containing calcium chloride was also joined to this U-tube. A thermometer was inserted through an opening at the top of the

* The dehydration was completed at 170°.

furnace just above the glass tube. Air-tight joints were secured, and blank experiments were previously conducted. The boat containing the salt was placed at the end furthest from the U-tube containing pumice stone. The heating was gradual, and began from the opposite end. A regular stream of dry air was passed through the combustion tube, and the water set free from the substance was condensed and collected in the weighed U-tube containing pumice stone soaked in sulphuric acid. It was finally weighed again, and the difference between the two weights gave the amount of water in the compound.

Compound $AgCN,Hg(CN)_2,4H_2O$.

To 100 c.c. of a solution of silver nitrate containing 12 grams of the salt was added a filtered solution of 6 grams of mercuric cyanide in 100 c.c. of water. This mixture was allowed to evaporate to half its original bulk. A slight turbidity was noticed almost from the beginning. From the ice-cold concentrated solution, milk-white needles were deposited within ten minutes. These were collected and washed, first with a little water, then with alcohol, and dried on a porous plate at 25°.

The compound decomposes slightly in the presence of water and dissolves in dilute sulphuric acid:

I. 0·8172 gave 0·2403 AgCl and 0·4166 HgS. Ag=22·12; Hg=43·94.

0·2735 gave 22·2 c.c. N_2 at 30° and 760 mm. CN=17·64.

II. 0·5797 gave 0·1751 AgCl and 0·2998 HgS. Ag=22·73; Hg=44·59.

0·7988 gave 0·1196 H_2O.* H_2O=14·97.

$AgCN,Hg(CN)_2,4H_2O$ requires Ag=23·5; Hg=43·66; CN=17·07; H_2O=15·77 per cent.

Action of Mercuric Cyanide on Chromium Trichloride and Vanadium Trichloride.

The action of mercuric cyanide on the above-mentioned salt solutions was tried in a similar manner, but the attempt to bring about a combination failed, and the product obtained in each case consisted of an oxide of the respective metal. The cyanides were no doubt formed at first, but these, being unstable, decomposed into

* The salt began to give off water from 85° onwards and the dehydration was completed at 180°.

the oxide and free hydrocyanic acid, the odour of the latter being distinctly perceptible. Thus:

A. $2CrCl_3 + 3Hg(CN)_2 + 6H_2O = 3HgCl_2 + 2Cr(CN)_3 + 6H_2O$.
$2Cr(CN)_3 + 6H_2O = 2Cr(OH)_3 + 6HCN$.

B. $2VCl_3 + 3Hg(CN)_2 + 3H_2O + O_2 = 3HgCl_2 + V_2O_5 + 6HCN$.

Action of Mercuric Cyanide on Ammonium Molybdate and Lead Nitrate.

These reactions also failed to yield the expected cyanides; with ammonium molybdate was obtained metallic mercury in the shape of fine globules, and the oxide, Mo_2O_5, as a violet-black powder, whilst in the latter case lead oxide was produced.

Compound $MnCl_2,Hg(CN)_2,2H_2O$.

About 25 grams of manganese chloride were dissolved in 150 c.c. of water, and a solution of mercuric cyanide (10:100) was added. The mixture was evaporated on the water-bath for one and a-half hours, and the bulk reduced to 100 c.c. This concentrated solution was well stirred and allowed to cool overnight. Next morning, a crystalline mass of pinkish-white scales had formed, which was powdered, washed with the mother liquor, and finally with alcohol. The compound was dried on a porous plate for two days at 24—25°. This salt was found to be dihydrated, whereas Poggiale described it as being trihydrated. It is very readily soluble in water, and under the microscope appears to consist of prismatic crystals:

I. 0·1617 gave 0·056 $Mn_2P_2O_7$ and 0·0918 HgS. Mn = 13·41; Hg = 48·97.
0·1617 gave 0·1197 AgCl. Cl = 18·32.
0·3274 ,, 18·8 c.c. N_2 at 24° and 760 mm. CN = 12·14.

II. 0·2084 gave 0·0724 $Mn_2P_2O_7$ and 0·1180 HgS. Mn = 13·44; Hg = 48·81.
0·2084 gave 0·1485 AgCl. Cl = 17·63.
0·8353 ,, 0·0780 H_2O. H_2O = 9·34.*

$MnCl_2,Hg(CN)_2,2H_2O$ requires Mn = 13·28; Hg = 48·30; Cl = 17·15; CN = 12·56; H_2O = 8·71 per cent.

The conductivity of the salt at different dilutions was determined.

* The salt began to give off water from 90° onwards. The dehydration was completed at 170°.

$T = 23°$.

Dilution. V.	Molecular conductivity. μ_v.	μ_v for zinc chloride.
50	204	207
100	212	216
500	237	231
1000	245	235

The molecular conductivity of zinc chloride at 23° for different dilutions is quoted from Kohlrausch's table, and proves to be almost identical with that of the salt. Assuming the molecular conductivity of zinc chloride and manganese chloride to be the same, as has been shown to be true by Kohlrausch, then the above compound evidently undergoes dissociation in solution into the ions $Mn^{\cdot\cdot}$ and Cl' and the undissociated molecule $Hg(CN)_2$. This is confirmed by the fact that when treated with silver nitrate, silver chloride, but no silver cyanide, is formed. The determination of the molecular weight of the compound by the cryoscopic method supports the above view.

Solvent, 19·86 grams of water.

	Solute.	Δt.	M.W.
1	0·4593	−0·40°	107·3
2	0·9031	−0·75	112·0

M.W. calculated for no dissociation = 414.
M.W. calculated for dissociation to $Mn^{\cdot\cdot}$, Cl_2'' and $Hg(CN)_2$ = 103·5.

Compound $4AlCl_3,HgCl_2,28H_2O$.

About 25 grams of hydrated aluminium chloride were dissolved in 100 c.c. of water, and a cold solution of 10 grams of mercuric cyanide in 100 c.c. of water was added. The mixture was evaporated to about 50 c.c., and as no deposit was obtained on allowing the solution to remain overnight, it was placed in a vacuum desiccator over sulphuric acid. After a day, a crystalline crust was found to have been formed on the surface of the solution. This was broken, and the crystallisation in a vacuum allowed to proceed for a further couple of days. During this interval, the crust on the surface was broken from time to time, and throughout the whole process of evaporation a strong odour of hydrocyanic acid was noticed. The crystals were collected, washed first with the mother liquor, and then repeatedly with alcohol. The compound was finally dried in a vacuum for two days:

I. 0·4973 gave 0·0877 HgS and 0·0804 Al_2O_3. Hg = 15·19; Al = 9·51.

0·4348 gave 0·6548 AgCl. Cl = 36·43.

II. 0·4407 gave 0·0777 HgS and 0·0790 Al_2O_3. Hg = 15·20; Al = 8·57.

0·5995 gave 0·8831 AgCl. Cl = 37·25.

$4AlCl_3,HgCl_2,28H_2O$ requires Hg = 15·27; Al = 8·25; Cl = 37·96; H_2O = 38·52 per cent.

Cryoscopic Determination of the Molecular Weight.

Solvent, 15·7251 grams of water.

	Solute.	Δ*t*.	M.W.
1	0·0963	−0·087°	130·84
2	0·3077	−0·277	130·94
3	0·6055	−0·515	137·10

The value found in this way approximates to one-tenth of the molecular weight, namely, 1309. In aqueous solution, the double salt is decomposed, as the solution is found to be distinctly acid. Since the compound $4AlCl_3,HgCl_2,28H_2O$ is completely hydrolysed to hydrochloric acid, aluminium hydroxide, and mercuric chloride, the observed molecular weight ought to be one-twelfth of 1309, as the lowering of the freezing point, due to the aluminium hydroxide and mercuric chloride, is quite negligible. This anomaly is difficult to explain, and the molecular weight determination does not, therefore, furnish much evidence as to the true molecular weight of the double salt in solution.

I avail myself of this opportunity to express my sincere thanks to Sir Prafulla Chandra Rây for his helpful interest and encouragement in this work.

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XI.—*Acyl Substituted* iso*Thiohydantoins.*

By Augustus Edward Dixon and Raymond Thomas Joachim Kennedy.

Concerning the acyl substituted *iso*thiohydantoins, practically the whole of our knowledge, embodied in two papers, one by Wheeler and Johnson (*Amer. Chem. J.*, 1902, **28**, 121) and the other by Johnson, Wallbridge, McFarland, and Cramer (*J. Amer. Chem. Soc.*, 1903, **25**, 483), may be summarised as follows. *iso*Thiohydantoins containing an aryl group, R, in the ring, by treatment with thiolacetic acid or with acetic anhydride, yield acetyl derivatives of the form $MeCO\cdot N{:}C<\begin{matrix}NR\cdot CO\\ S\text{——}CH_2\end{matrix}$, the phenylic member of this class being producible also from either phenyl*iso*thiohydantoïc acid or thiocyanoacetanilide by means of acetic anhydride. Further, ordinary β-naphthyl*iso*thiohydantoïn gives with acetic anhydride a derivative, $C_{10}H_7\cdot N{:}C<\begin{matrix}N(COMe)\cdot CO\\ S\text{————}CH_2\end{matrix}$, the corresponding *o*- or *p*-tolyl*iso*thiohydantoin, under like treatment, affording a diacetyl derivative.

No purely acidic substitution derivative of *iso*thiohydantoin seems yet to have been described. It was found, too, by Dixon and Taylor (T., 1912, **101**, 558) that *ab*-acetylphenylthiocarbamide, when heated with chloroacetyl chloride, yields ordinary phenyl*iso*thiohydantoin, the acyl substituent of the thiocarbamide being expelled in the form of acetyl chloride. Similar results were observed with tri-substituted thiocarbamides containing the acetyl, the benzoyl, or the carbethoxy-radicle, together in each case with two hydrocarbon residues.

Such tri-substitution derivatives are not particularly stable. More recent investigation has shown that less highly substituted thiocarbamides containing the group ·CO·OR (where R = alkyl or aryl), by means of chloroacetyl chloride are transformable into *iso*thiohydantoins without the loss of that group. Thus, for example, carbethoxy*iso*thiohydantoin may be obtained from carbethoxythiocarbamide, or a phenylcarbethoxy-analogue from *ab*-phenylcarbethoxythiocarbamide.

Consistently with the observations of Dixon and Taylor (*loc. cit.*) it has been found that ethyl chloroacetate, in alcoholic solution, fails to attack the *mono*-substituted carboalkyloxythiocarbamides; if, however, calcium carbonate is added to the mixture, interaction takes place, with the formation of the corresponding mono-substi-

tuted *iso*thiohydantoins. With di-substituted thiocarbamides, $RO\cdot CO\cdot NH\cdot CS\cdot NHPh$, or with mono-substituted carboaryloxythiocarbamides, however, ethyl chloroacetate does not react, either directly or in the presence of calcium carbonate.

So far as their method of production is concerned, the carboalkyloxy*iso*thiohydantoins referred to above might have either (or both) of the configurations represented by the formulæ:

$$RO\cdot CO\cdot N{:}C{<}\begin{matrix}NPh\cdot CO\\ S\text{——}CH_2\end{matrix} \quad \text{and} \quad PhN{:}C{<}\begin{matrix}N(CO_2R)\cdot CO\\ S\text{————}CH_2\end{matrix}$$

(I.) (II.)

When hydrolysed by means of hot dilute hydrochloric acid, they yield carbon dioxide, ammonium chloride, and 'phenyldioxythiazole.' Now, Dixon has shown (T., 1897, **71**, 623) that in the transformation by which a substituted *iso*thiohydantoin furnishes a substituted 'dioxythiazole,' the nitrogen member of the parent ring is exchanged for an oxygen atom, thus:

$$RN{:}C{<}\begin{matrix}NH\cdot CO\\ S\text{——}CH_2\end{matrix} \xrightarrow{H_2O} RN{:}C{<}\begin{matrix}O\cdot CO\\ S\cdot CH_2\end{matrix} + NH_3,$$

whence it follows that the foregoing carboalkyloxy*iso*thiohydantoins have the constitution represented by formula II.

Judgment in the case of mono-substitution derivatives is a less simple matter. Analogy would suggest the formula

$$NH{:}C{<}\begin{matrix}N(CO_2R)\cdot CO\\ S\text{————}CH_2\end{matrix},$$

which also is consistent with the fact that, on hydrolysis by acid, they rapidly yield carbon dioxide, ammonia, and dioxythiazole. Moreover, that the latter does not result through the hydrolysis of *iso*thiohydantoin, possibly formed from a compound,

$$RO\cdot CO\cdot N{:}C{<}\begin{matrix}NH\cdot CO\\ S\text{——}CH_2\end{matrix},$$

is clear; because, whilst the actual hydrolysis is speedily accomplished, that of *iso*thiohydantoin, in like circumstances, is very slow, yet the presence of this compound could not be detected in the mixture. Nevertheless, it is conceivable that a substituted dioxythiazole, $CO_2R\cdot N{:}C{<}\begin{matrix}O\cdot CO\\ S\cdot CH_2\end{matrix}$, might be formed and then hydrolysed, with elimination of the group $\cdot CO_2R$. Substances of the class last formulated are unknown.

Through the action of chloroacetyl chloride on *a*-acetyl-*b*-carbethoxythiocarbamide it should be possible to synthesise a compound having the structure $CO_2Et\cdot N{:}C{<}\begin{matrix}NH\cdot CO\\ S\text{——}CH_2\end{matrix}$, and if this should

prove isomeric with that from carbethoxythiocarbamide itself, decision would be easy. In practice, however, such a check could not be applied, all attempts to produce a thiocarbamide of the required configuration being unsuccessful.

Experimental.

*Phenylcarbethoxy*iso*thiohydantoin.*

When *ab*-phenylcarbethoxythiocarbamide was heated on the steam-bath with slightly more than one molecular proportion of chloroacetyl chloride, liquefaction occurred with disengagement of hydrogen chloride and rapid deposition of a brown solid, the action being complete within a few minutes.

By recrystallisation from hot glacial acetic acid, which dissolves it freely, the product was obtained in white needles, sparingly soluble in boiling alcohol, benzene, acetone, or cold acetic acid, and commencing to decompose at about 220°, but melting only towards 250°. The substance is very slowly desulphurised by boiling with the alkaline solution of a lead salt, but readily yields silver sulphide when heated with ammoniacal silver nitrate. That it contains the group $\cdot S\cdot CH_2\cdot CO\cdot$ was shown by boiling the substance with alcoholic potassium hydroxide, acidifying the liquor, and mixing with ferric chloride, followed by ammonia, the resultant purple coloration indicating (Andreasch, *Ber.*, 1879, **12**, 1385) the presence of α-thiolacetic acid.

Found: N = 10·58; S = 12·2.

$C_{12}H_{12}O_3N_2S$ requires N = 10·60; S = 12·12 per cent.

A mixture of ethyl chloroacetate and *ab*-phenylcarbethoxythiocarbamide, in alcoholic solution, was boiled for three hours under reflux with excess of calcium carbonate, and filtered whilst hot. From the filtrate, as it cooled, the unchanged thiocarbamide separated in crystals, and the mother liquor gave no reaction for α-thiolacetic acid; in these circumstances, therefore, neither an *iso*thiohydantoin nor an *iso*thiohydantoic acid had been formed.

Hydrolysis.—Hot concentrated hydrochloric acid rapidly dissolved the substance, carbon dioxide being evolved, and from the solution, as it cooled, 'phenyldioxythiazole' separated in long, flattened prisms melting at 143—144°. In different experiments the yield varied from 60 to 80 per cent. of the theoretical.

The acid liquor from which the crystals had been deposited gave, on evaporation, ammonium chloride together with a little aniline hydrochloride. As phenyldioxythiazole itself yielded no aniline when heated with hydrochloric acid, it is possible that the *iso*thio-

hydantoin, $PhN{:}C\genfrac{}{}{0pt}{}{<N(CO_2Et)\cdot CO}{<S\text{———}CH_2}$, contained a trace of the isomeride, $CO_2Et\cdot N{:}C\genfrac{}{}{0pt}{}{<NPh\cdot CO}{<S\text{——}CH_2}$, from which aniline would be producible.

*Phenylcarbomethoxy*iso*thiohydantoin.*

This was prepared in the manner already described, but from *a*-phenyl-*b*-carbomethoxythiocarbamide, and was similarly recrystallised from acetic acid. Marked decomposition occurred during the preparation, and the yield was poor. Except that the compound was rather more readily soluble in cold acetic acid, it resembled alike in properties and in reactions the carbethoxy-homologue; when heated, it decomposed gradually, but did not melt, even at 250°.

Found: S = 12·45.

$C_{11}H_{10}O_3N_2S$ requires S = 12·8 per cent.

*Phenylcarboxy-o-tolyl*iso*thiohydantoin.*

a-Phenyl-*b*-carboxy-*o*-tolylthiocarbamide (7·6 grams), in dry benzene, was heated for three hours, under reflux, with excess of chloroacetyl chloride. On cooling, crystals were deposited which, after recrystallisation from alcohol, weighed 1·3 grams, the original mother liquor, when evaporated, giving 3·5 grams of unchanged thiocarbamide; the yield, therefore, was but 28 per cent. of the theoretical.

Found: N = 8·42; S = 9·85.

$C_{17}H_{14}O_3N_2S$ requires N = 8·59; S = 9·82 per cent.

The substance occurred in white, rectangular prisms, sparingly oluhle in cold alcohol or benzene, and melting at 169—170°. Deulphurisation by boiling with the alkaline solution of a lead salt ras slow and imperfect, even on prolonged boiling; but, with hot mmoniacal silver nitrate, blackening took place readily. By hot lcoholic potassium hydroxide α-thiolacetic acid was produced, and ecognised by Andreasch's method; owing, however, to lack of aterial, no further experiments could be made towards deciding ne constitution of the substance.

The original thiocarbamide, when boiled with ethyl chloroacetate nd alcohol in the presence of calcium carbonate, afforded not a ace of the above *iso*thiohydantoin.

*Carbethoxy*iso*thiohydantoin.*

Carbethoxythiocarbamide and chloroacetyl chloride were heated with benzene under reflux until hydrogen chloride ceased to escape, the action being complete in about three hours. During the process a yellow solid was deposited, consisting of the impure hydrochloride of the above base, which latter was obtained by dissolving the product in hot acetic acid, filtering off any hydrochloride that separated on cooling, and evaporating the filtrate in a vacuum. More readily, it is obtainable from the crude hydrochloride by recrystallisation from alcohol, mixed with finely divided calcium carbonate.

When ethyl chloroacetate was used, instead of chloroacetyl chloride, no sign of interaction was detectable after three hours' boiling; but when the experiment was repeated with an alcoholic solution in the presence of calcium carbonate, this being filtered off at the end of one and a-half hours, the filtrate, on cooling, deposited the nearly pure base.

*Carbethoxy*iso*thiohydantoin* separates from alcohol in white, hard, felted needles, melting and decomposing at 173—174°; it is sparingly soluble in cold water, moderately soluble in methyl alcohol, more readily so in ethyl alcohol, and dissolves freely in glacial acetic acid. It is not desulphurised by boiling with the alkaline solution of a lead salt or with ammoniacal silver nitrate, but is hydrolysed by hot alcoholic potassium hydroxide, with the formation of α-thiolacetic acid.

Found: N = 14·84; S = 17·11.

$C_6H_8O_3N_2S$ requires N = 14·90; S = 17·02 per cent.

Hot dilute hydrochloric acid readily dissolved the substance, with effervescence due to the escape of carbon dioxide, and from the solution, when it had been evaporated down to a small bulk, crystals were deposited melting at 120—125° and consisting of nearly pure dioxythiazole.

The *hydrochloride* formed cream-white needles, commencing to decompose at about 160°, but not melting at 200°. Insoluble in benzene, it dissolves in hot acetic acid with the loss of part, but not all, of the combined hydrogen chloride. By dissolution in hot water it is rapidly and completely decomposed, the liberated acid converting the base into dioxythiazole; with boiling alcohol the same change occurs, but more slowly.

Found: S = 14·62.

$C_6H_8O_3N_2S,HCl$ requires 14·25 per cent.

*Carbomethoxy*iso*thiohydantoin.*

From carbomethoxythiocarbamide, in benzene, and chloroacetyl chloride the hydrochloride was obtained as in the last preparation, and on recrystallisation from acetic acid gave the pure base. Similarly, from the above thiocarbamide and ethyl chloroacetate in the presence of calcium carbonate (but not in its absence) the free base was obtained.

In respect of general properties and reactions, carbomethoxy*iso*thiohydantoin closely resembles the carbethoxy-homologue, being, however, somewhat less readily soluble in methyl alcohol, ethyl alcohol, or glacial acetic acid. It has no definite melting point, but decomposes from about 170° onwards, being still unmelted at 220°.

Found: N = 16·05; S = 18·24.

$C_5H_6O_3N_2S$ requires N = 16·09 S = 18·39 per cent.

On contact with hot dilute hydrochloric acid, it dissolved with escape of carbon dioxide, the solution, when evaporated, giving ammonium chloride, together with dioxythiazole. (Found, S = 26·85; dioxythiazole requires S = 27·35 per cent.)

By alkaline hydrolysis it yielded α-thiolacetic acid, which was recognised as before.

*Carbophenoxy*iso*thiohydantoin.*

Carbophenoxythiocarbamide in dry benzene, when heated under reflux with chloroacetyl chloride, gave a yellow, crystalline mass of the substituted *iso*thiohydantoin hydrochloride. By treatment with boiling alcohol containing finely divided calcium carbonate in suspension, the free base was obtained in faintly yellow crystals melting at 185—186°.

Found: S = 13·51.

$C_{10}H_8O_3N_2S$ requires S = 13·56 per cent.

Hydrolysis with hot alcoholic potassium hydroxide gave a solution responding to Andreasch's test for α-thiolacetic acid.

With the foregoing thiocarbamide, in alcohol, ethyl chloroacetate failed to react, even in the presence of calcium carbonate—a result differing sharply from that observed with the carbethoxy- or with the carbomethoxy-analogue. The experiment was repeated, carbo-*o*-tolyloxythiocarbamide being used instead, but in this case, too, no interaction took place.

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XII.—*Carboalkyloxythiocarbamides.*

By Augustus Edward Dixon and Raymond Thomas Joachim Kennedy.

In the course of a recent investigation (see preceding paper), progress was much retarded through the difficulty experienced in preparing sufficient quantities of certain necessary thiocarbamides, particularly those containing the carbomethoxy- or the carbethoxy-group, alone. Although such compounds are known, having been obtained both from the corresponding thiocarbimides and ammonia (Doran, T., 1896, **69**, 331) and by the hydrolysis of aldehyde–ammonia derivatives of the former (Dixon and Taylor, T., 1916, **109**, 1260), the yields are far from satisfactory—at all events, the best yield now attained by either method did not exceed 5 per cent. of the theoretical.

From *ab*-acetylphenylthiocarbamide, by heating it with excess of ethyl chlorocarbonate, the acetyl radicle is expelled as chloride, with the formation of the corresponding *ab*-carbethoxyphenylthiocarbamide (Doran, T., 1901, **79**, 913); it seemed, therefore, almost a foregone conclusion that from acetylthiocarbamide, in like circumstances, the products must be acetyl chloride and carbethoxythiocarbamide, $NH_2\cdot CS\cdot NH\cdot CO_2Et$. This forecast proved incorrect, for, on experiment, no trace of the latter substance was obtained.

By treating with dilute alkali hydroxide the additive compound of a hydrocarbon mono-substituted thiocarbamide and a chlorocarbonate, Dixon succeeded in realising the changes

$$\begin{matrix}R\cdot NH \\ NH_2\end{matrix}\!\!>\!C{:}S\!<\!\!\begin{matrix}CO_2Et \\ Cl\end{matrix} \longrightarrow \begin{matrix}R\cdot N \\ NH_2\end{matrix}\!\!>\!CS\cdot CO_2Et \longrightarrow NH_2\cdot CS\cdot NR\cdot CO_2Et$$

on the other hand, the corresponding, non-substituted base,

$$\begin{matrix}NH \\ NH_2\end{matrix}\!\!>\!C{:}S\cdot CO_2Et,$$

when similarly liberated from its 'hydrochloride,' broke down without yielding carbethoxythiocarbamide (T., 1903, **83**, 558, 565).

In the last case, the attack of the alkali hydroxide being primarily on the carbethoxy-group, it seemed probable that if alkali bicarbonate were used instead of alkali hydroxide, the disruption of that group might at least be hindered for a while. If so—the speed of migration of an acyl radicle from sulphur to nitrogen being often a matter of seconds—even a slight delay in the breaking down of the carbethoxy-complex might leave time enough for its transference.

Experimentally, this prevision has been justified by the production of the compounds sought, namely, carbomethoxy- and carbethoxy-thiocarbamides; they have been obtained, however, only indirectly, and through some unexpected intermediate reactions. Briefly, the facts are as follows.

Thiocarbamide–ethyl chlorocarbonate, $\frac{NH_2}{NH_2}\!>\!C{:}S\!<\!\frac{CO_2Et}{Cl}$, in aqueous solution yields with sodium hydrogen carbonate a bulky, white precipitate of the corresponding bicarbonate,

$$\frac{NH_2}{NH_2}\!>\!C{:}S\!<\!\frac{CO_2Et}{O\cdot CO_2H},$$

an unstable compound, which soon changes into a compact mass of prisms consisting of *aa*-dicarbethoxythiocarbamide; concurrently, thiocarbamide is liberated and passes into solution, along with the sodium chloride. The dicarbethoxythiocarbamide, itself stable, is readily hydrolysed in alcoholic solution by hydrochloric acid, with the formation of the monocarbethoxy-derivative,

$$NH_2{\cdot}CS{\cdot}NH{\cdot}CO_2Et.$$

Although the bicarbonate soon decomposes, especially in the presence of water, the change requires a certain time, and the bulky precipitate, if treated at once with dilute hydrochloric acid, dissolves, thereby furnishing a clear solution of the original salt (thiocarbamide–ethyl chlorocarbonate, in aqueous solution, gives a picrate identical with that obtained from the above solution of the bicarbonate in acid). The bicarbonate, after some twenty-four hours' keeping in a desiccator, changed completely into a mixture of thiourea and dicarbethoxythiocarbamide.

Thiocarbamide–methyl chlorocarbonate behaves similarly.

The spontaneous change of a salt containing but one carbethoxy- (or carbomethoxy-) group into an *aa*-di-substituted thiocarbamide is a remarkable phenomenon. That the last-named substance really has the *aa*-configuration follows from experimental results, that will presently be stated; moreover, that it is no mere by-product is clear, for, reckoned on the weight of 'hydrochloride' employed and calculated from the equation

$$2\frac{NH_2}{NH_2}\!>\!C{:}S\!<\!\frac{CO_2Me}{O\cdot CO_2H} \longrightarrow NH_2{\cdot}CS{\cdot}N(CO_2Me)_2 + CSN_2H_4 + 2H_2CO_3,$$

the yield of di-substitution derivative may reach at least 70 per cent. of the theoretical.

As regards the migration of an acyl group from sulphur to nitrogen, the process is of a kind now well established as normal. Further, if one of the two nitrogen atoms of the acyl-ψ-thiocarbamide is charged already with a hydrocarbon radicle, the wander-

ing acyl group goes always to join the latter (see, for example, Dixon and Hawthorne, T., 1907, **91**, 128), and may either remain there permanently, or may again move, spontaneously or under stress, to the other; but, to the already substituted nitrogen atom, it goes in the first instance. Consequently, if the group $\cdot CO_2R$ has made its normal excursion to yield the substituted thiocarbamide, $NH_2\cdot CS\cdot NH\cdot CO_2R$, it seems natural that a second, following in after the first, should take up the same station, at all events temporarily. In the case here considered, one may reasonably suppose that the second radicle is furnished by another molecule of the base, $NH_2\cdot C(:NH)\cdot S\cdot CO_2R$, which holds it only loosely; and the fact that thiourea, not initially present, is fonnd eventually along with the di-substitution product, is consistent with such a view. Still, it is a curious change, and all attempts hitherto made to reproduce it with other acyl sulphonium salts have proved unsuccessful.

For the structure, $NH_2\cdot CS\cdot N(CO_2R)_2$, assigned to the foregoing dicarboalkyloxythiocarbamides, the experimental evidence is that the dicarbethoxy-compound, hy cold concentrated alkali hydroxide, is resolved into thiocyanic acid and the ethyl ester of iminodicarbouic acid,

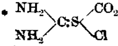
$$NH_2\cdot CS\cdot N(CO_2Et)_2 \longrightarrow HSCN + NH(CO_2Et)_2.$$

Those *aa*-derivatives are white. According to E. A. Werner (T., 1916, **109**, 1124), the yellow diacetylthiourea, obtained from acetic anhydride and thiourea in the presence of a mineral acid, is a ψ-thiocarbamide, $MeCO\cdot NH\cdot C(:NH)\cdot S\cdot COMe$. Whether this really expresses the constitution of the compound, it is somewhat difficult to judge from the evidence adduced, since part of the latter—notably the decomposition, by heat, into acetamide and acetylthiocarbimide—would equally well support the *ab*-formula. In the present connexion, however, the sole point of interest was to learn whether the two acyl radicles might possibly he attached to the same nitrogen atom. On treatment with concentrated alkali hydroxide, however, the diacetyl compound afforded not a trace of thiocyanic acid, a result decisive against that view.

EXPERIMENTAL.

Carbethoxy-derivatives.

To a concentrated aqueous solution of thiocarbamide–ethyl chlorocarbonate,* sodium hydrogen carbonate was added in slight

* . This name is not quite so cumbrous as diaminomethylenecarbethoxysulphonium chloride. Besides, it is not impossible that the compound may be an ammonium salt.

excess; carbon dioxide was rapidly evolved, a crystalline material being deposited, which, after it had remained for some time, was collected, washed, and dried. The product formed shining, white, rectangular plates melting at 97° with effervescence, and with the evolution of carbethoxythiocarbimide, easily recognised by its characteristic odour. Practically insoluble in water or in benzene, it dissolved freely in alcohol, the solution giving with ammoniacal silver nitrate a black precipitate of silver sulphide, but resisting desulphurisation by the alkaline solution of a lead salt, even after prolonged boiling. Analysis showed the compound to be a dicarbethoxythiocarbamide.

Found: N=12·64; S=14·44.

$C_7H_{12}O_4N_2S$ requires N=12·73; S=14·54 per cent.

In cold concentrated alkali hydroxide, the substance dissolved readily, a portion of the liquid, when acidified and then treated with ferric chloride, giving the reaction of thiocyanic acid. From the remainder, ether extracted a material having the properties and giving the reactions of diethyl iminodicarbonate (Found: N=8·68. $C_6H_{11}O_4N$ requires N=8·69 per cent.).

When allowed to evaporate spontaneously, the liquor from which the dicarbethoxythiocarbamide had separated left a residne of sodium chloride mixed with thiourea.

Dicarbethoxythiocarbamide is practically insoluble in dilute hydrochloric acid. Yet the precipitate obtained by means of sodium hydrogen carbonate, if treated immediately with a dilute acid, dissolved at once, and the solution gave with picric acid a sparingly soluble, bright yellow *picrate* melting at 150—151°. From an aqueous solution of thiocarbamide–ethyl chlorocarbonate, a picrate was obtained having the same melting point, and a mixture of the two, in equal proportions, melted also at 150—151°; evidently, the bicarbonate precipitate, when freshly prepared, is transformable into the salt from which it was generated.

That precipitate, originally voluminous, but shrinking as it changes into the thiocarbamide, was supposed at first to he the free base, carbethoxy-ψ-thiocarbamide, $NH_2·C(:NH)·S·CO_2Et$. Strange to say, this is not so; it is an unstable salt, apparently the bicarbonate of the base. When filtered off as rapidly as possible, washed with acetone, and dried in bibulous paper, it formed rectangular plates, melting and effervescing at 59—60°, having a distinct odour of carbethoxythiocarbimide, and dissolving in acid with the evolution of carbon dioxide to a clear solution; in plain water it dissolved appreciably, but without effervescence.

Found: N=15·2; S=16·4.

$C_5H_{10}O_3N_2S$ requires N=15·64; S=17·87 per cent.

Naturally, the experimental figures are no more than roughly approximate to those calculated. After twenty-four hours' keeping in a vacuum desiccator, the substance had completely decomposed into a mixture (m. p. 70—100°), from which water extracted a portion, leaving a residue of slightly impure dicarbethoxythiocarbamide. The aqueous extract, when treated with hydrochloric acid and potassium nitrite, followed by picric acid, yielded the picrate of formamidine disulphide, recognised by its melting point and by the mixed melting-point method; hence it contained thiourea. Neither carbethoxythiocarbamide nor *aa*-dicarbethoxythiocarbamide yields a derivative of formamidine disulphide under the above conditions, nor does either of them give a picrate with aqueous picric acid.

Further to confirm that the unstable substance is a carbonate (and not the corresponding free base), a quantity of the freshly prepared material, in aqueous solution, was mixed with a clear solution of basic lead acetate, whereon lead carbonate was precipitated. To the filtrate, freed from most of the lead by means of hydrochloric acid, and subsequent filtration, picric acid was added, the picrate of carbethoxy-ψ-thiocarbamide (see above) thus being obtained.

Carbethoxythiocarbamide is formed when a solution of *aa*-dicarbethoxythiocarbamide, in alcohol, is acidified with hydrochloric acid; on keeping, the former gradually separates in crystals, the yield being about 80 per cent. of that required by the equation

$$NH_2\cdot CS\cdot N(CO_2Et)_2 + H_2O \longrightarrow NH_2\cdot CS\cdot NH\cdot CO_2Et + CO_2 + EtOH.$$

More easily, it may be obtained by adding excess of sodium hydrogen carbonate to an alcoholic solution of thiocarbamide–ethyl chlorocarbonate, and shaking the mixture from time to time; when the reaction is at an end, the turbid mixture is filtered, the filtrate being then acidified and set aside for the crystals to separate. Although, in relation to the amounts of thiocarbamide and of ethyl chlorocarbonate originally taken, the yield is not very gratifying, yet, compared with that of the methods earlier mentioned, it is highly productive; the process, too, is facile of operation, because the 'hydrochloride' may be obtained by passing carbonyl chloride through a suspension of thiourea in benzene and absolute alcohol (compare T., 1903, **83**, 565).

Carbomethoxy-derivatives.

Thiocarbamide–methyl chlorocarbonate, in aqueous solution, gave with sodium hydrogen carbonate a bulky, white precipitate, melting at 62·5—63·5°, and resembling in general properties the carbethoxy-homologue, except for a slightly greater solubility in water. The

freshly prepared hydrogen carbonate, $\frac{NH_2}{NH_2}>C:S<\frac{CO_2Me}{O \cdot CO_2H}$, dissolved readily and completely in cold dilute hydrochloric acid, the solution yielding with picric acid a sparingly soluble, bright yellow *picrate* melting at 207—210°.

Found: N = 14·72; S = 17·44.

$C_4H_8O_5N_2S$ requires N = 14·28; S = 16·33 per cent.

To measure the carbon dioxide, a portion was treated in the Lunge nitrometer, over mercury, with excess of dilute hydrochloric acid.

Found: CO_2 = 21·65. Theory requires CO_2 = 22·45 per cent.

Decomposition was slower than in the case of the carbethoxy-derivative, the solid, even after twenty-four hours' keeping, still effervescing slightly on acidification; at the end of two days, however, the change was complete. By means of cold water, the thiourea was extracted, a mass of white, rhombic plates being left; they were readily soluble in alcohol, but practically insoluble in water, ether, acetone, benzene, or light petroleum, and melted at 117—118°.

Found: N = 14·44; S = 16·54.

$C_5H_8O_4N_2S$ requires N = 14·58; S = 16·67 per cent.

Reckoned from the weight of thiocarbamide–methyl chlorocarbonate employed, the yield of dicarbomethoxythiocarbamide was about 70 per cent. of the theoretical.

In cold concentrated alkali hydroxide, the substance dissolved at once, the solution reacting copiously for thiocyanic acid; hence both carbometboxy-groups are attached to the same nitrogen atom.

The alcoholic solution, when acidified with hydrochloric acid, gradually deposited crystals of carbomethoxythiocarbamide. In this case, however, as in that of the higher homologue, it is unnecessary to prepare the *aa*-compound; an alcoholic solution of thiocarbamide–methyl chlorocarbonate (which may be prepared from thiourea in methyl alcohol–benzene suspension and carbonyl chloride), when treated with sodium hydrogen carbonate and then acidified, gives the mono-substitution derivative in yield varying from 60 to 70 per cent. of the theoretical.

A solution of thiocarbamide–methyl chlorocarbonate in water remained practically clear after some weeks' keeping, and hence had developed neither carbomethoxy- nor dicarbomethoxy-thiocarbamide. Decomposition slowly occurred, partly with regeneration of thiourea and partly with the formation of the hydrochloride of methyl-ψ-thiocarbamide, $NH_2 \cdot C(:NH) \cdot SMe$.

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XIII.—*Organic Derivatives of Tellurium. Part I. Dimethyltelluronium Dihaloids.*

By Richard Henry Vernon.

The first mention of dimethyltelluronium di-iodide, $TeMe_2I_2$, is by Demarçay (*Bull. Soc. chim.*, 1883, [ii], **40**, 99), who merely states that this substance is obtained by the action of methyl iodide on tellurium, and that decomposition takes place at 100—120°.

In 1904, Scott (P., 1904, **20**, 157) confirmed Demarçay's work, mentioned that neither sulphur nor selenium behaves in a similar manner, and described the preparation of trimethyltelluronium iodide.

The present paper is more in the nature of an introduction to the chemistry of this singular di-iodide, and its main object is to show that there are not only two dimethyltelluronium di-iodides, two dibromides, and two dichlorides, but that these haloid derivatives of the bivalent radicle "dimethyltelluride" are respectively isomeric.

The reason for this duplication is that there are two bases, and that each base gives a corresponding series of derivatives.

The first, or α-base, is obtained by treating Demarçay's red iodide with silver oxide and water. An aqueous solution with markedly basic properties results.

To prepare the second, or β-base, the solution of the α-base is evaporated to dryness under specified conditions, and the white, crystalline mass redissolved in water.

The chemical behaviour towards reagents of these two bases is shown in the following table, the solutions in each case being precisely of the same concentration.

Reagent	Aqueous solution of α-base.	Aqueous solution of β-base.
$AgNO_3$	Precipitate of Ag_2O.	White precipitate. Becomes black on boiling.
$FeCl_3$	Precipitate of $Fe(OH)_3$ when base is in excess.	White precipitate when base is in excess.
$FeCl_3$	A red solution becoming darker on boiling.	No precipitate when $FeCl_3$ is in excess.
H_2PtCl_6	No precipitate.	Yellow platinum salt.
Picric acid	No precipitate.	Yellow picrate.

The best reaction to distinguish between them is that with silver nitrate, and tbis first directed the author's attention to their existence. Another typical reaction is with ferric chloride. Both these bases form picrates, but that of the α-base possesses a much greater solubility than that derived from the β-base. Generally speaking, the two bases behave towards metallic salts like the alkalis, the precipitates being apparently similar in some cases, but showing marked differences in others.

Apart from these reactions, the chief feature of interest lies in the action of the halogen acids.

Thus, if the α-base is treated with hydriodic acid, the original α-iodide, namely, Demarçay's, is regenerated.

$$\underset{\alpha\text{-Iodide.}}{TeMe_2I_2} \xrightarrow{Ag_2O} \underset{\alpha\text{-Base.}}{TeMe_2(OH)_2} \xrightarrow{HI} \underset{\alpha\text{-Iodide.}}{TeMe_2I_2}$$

On treatment of the β-base with hydriodic acid, in marked contrast to the α-, Demarçay's iodide is not regenerated, but a new iodide totally different in chemical and physical properties, and this new or β-iodide has proved to be isomeric with the α- or Demarçay's iodide. The equation now becomes:

$$\underset{\alpha\text{-Iodide.}}{TeMe_2I_2} \xrightarrow{Ag_2O} \underset{\alpha\text{-Base.}}{TeMe_2(OH)_2} \xrightarrow{\text{evap.}} \underset{\beta\text{-Base.}}{TeMe_2(OH)_2} \xrightarrow{HI} \underset{\beta\text{-Iodide.}}{TeMe_2I_2}$$

Repeated attempts have so far shown that, although the α-base easily changes into the β-, the reverse is not the case. Furthermore, each iodide is converted into its corresponding base on treatment with silver oxide, and hence the still more generalised equation can be written:

$$\underset{\alpha\text{-Haloid.}}{TeMe_2X_2} \underset{HX}{\overset{Ag_2O}{\rightleftharpoons}} \underset{\alpha\text{-Base.}}{TeMe_2(OH)_2} \xrightarrow{\text{evap.}} \underset{\beta\text{-Base.}}{TeMe_2(OH)_2} \underset{Ag_2O}{\overset{HX}{\rightleftharpoons}} \underset{\beta\text{-Haloid.}}{TeMe_2X_2}$$

where X is either chlorine, bromine, or iodine, precisely the same reactions taking place with the other two halogen acids as with hydriodic acid itself.

There are thus six dimethyltelluronium dihaloids of the general type $TeMe_2X_2$, and in future all derivatives of the α-base will be prefixed by the letter α and those of the β-hase by the letter β.

This is very necessary, because not only do the two haloid series exist, but every salt is duplicated. This does not imply, however, that they are necessarily isomeric.

Melting Points.—The following is a comparison of the melting points:

α-Chloride : 92°	β-Chloride : 134°
α-Bromide : 92°	β-Bromide : 142°
α-Iodide : 127°	β-Iodide : (no m. p.)

Of these, the α-chloride and bromide melt sharply without decomposition, and the remainder decompose on fusion. The β-iodide imperceptibly changes into tellurium and methyl iodide above 100°, but no sign of fusion is observed.

Colour and Absorption Spectra.—Solutions of the dimethyltelluronium dihaloids have somewhat different colours from the salts themselves, and this is particularly marked with the two iodides.

The bright red crystals of the α-iodide give a deep orange solution, and the black or greenish-black crystals of the β-iodide a blood-red one. The following table gives the colour of the salts and their solutions:

	Salt.	Solution (*N*/100 in ethyl alcohol).
α-Chloride	Colourless.	Colourless.
β-Chloride	Tinged.	Tinged.
α-Bromide	Yellowish.	Yellowish.
β-Bromide	Orange	Orange.
α-Iodide	Red.	Deep orange.
β-Iodide	Black (greenish-black).	Blood-red.

Of considerable interest is the absorption spectra in the ultraviolet region, photographs of which were obtained through the

Salt.	Thickness of solution.	λ
α-Chloride	2 mm.	2640
	10 ,,	2742
	20 ,,	2760
	30 ,,	2780
β-Chloride	2 mm.	2680
	10 ,,	2750
	20 ,,	2890
	30 ,,	2935
α-Bromide	2 mm.	3005
	10 ,,	3245
	20 ,,	3300
	30 ,,	3350
β-Bromide	2 mm.	3045
	10 ,,	3310
	20 ,,	3405
	30 ,,	3450
α-Iodide	2 mm.	3940
	10 ,,	4190
	20 ,,	4320
	30 ,,	4425
β-Iodide	2 mm.	4350
	4 ,,	4425

kindness of Mr. J. E. Purvis. Hundredth-mol. solutions, in ethyl alcohol, were used in each case, and fifteen photographs were taken on each plate. The source of illumination was a cadmium spark, and the exposure was two minutes for each photograph. In no case were any bands observed, and the positions where general absorption began are given for thicknesses of 2, 10, 20, and 30 mm.

It will be noticed that (1) the β-haloid has a greater absorbing power than the corresponding α-one, and (2) the α-chloride shows the least absorption and the β-iodide the greatest, the latter absorbing to the extent of complete extinction through a thickness of solution greater than 4 mm.

In view of the enormous absorbing power of the two iodides, and especially of the β-iodide, two extra spectrographs were taken using a ten-thousandth-mole solution (ethyl alcohol), otherwise precisely the same conditions were maintained, and although a marked difference between the two was still noticeable, no bands were apparent.

Constitution.—(1) The existence of two series of dimethyltelluronium dihaloids has been established. In the case of each of the chlorides, bromides, and iodides it has been shown* (i) that they have the same percentage composition, (ii) that they have the same molecular weight, and (iii) that there is no question of polymorphism, since (*a*) the absorption spectra are different, and (*b*) their chemical behaviour is different, thus each regenerates its respective base when treated with silver oxide. The conclusion is, therefore, that these haloids must be respectively isomeric.

(2) Since in the α- as well as in the β-series both halogens are ionisable, the halogen being precipitated quantitatively by silver nitrate, and both the α- and the β-bases are strongly diacidic, the haloids of both series must be represented by structural formulæ of the type $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!Te\!<\!\begin{matrix}X\\X\end{matrix}$.

(3) The fact that there exist in these simple compounds of quadrivalent tellurium two substances corresponding with one structural formula shows that the relationship between the four tellurium valencies must be different from that generally assumed to exist between the carbon valencies in such a compound as methylene iodide, that is, there cannot be four equal valencies directed towards the solid angles of a regular tetrahedron of which the tellurium atom occupies the centre.

* Analytical figures and molecular weights will be found in the experimental part.

(*a*) The four tellurium valencies might have different values and not be equivalent to one another.

(*b*) Their arrangement might differ widely from the regular tetrahedral disposition. The most symmetrical disposition that would account for the existence of the two isomerides would be that in which the four valencies are in one plane.

(*c*) Another suggestion that might be put forward is that the tellurium atom occupies the apex of a pyramid with a rectangular base.

(4) The discussion of the exact cause of the isomerism will be fully dealt with in a later paper. The purpose of the present communication is merely to show that the compounds $TeMe_2X_2$ actually exist in two isomeric forms.

EXPERIMENTAL.

The α- or Demarçay's Iodide (α-Dimethyltelluronium Di-iodide).

According to Demarçay, this substance is obtained directly by heating at 80° a mixture of methyl iodide and tellurium in the proportion of two mols. of the former to one of the latter.

The best method of procedure is to blow a 150—200 c.c. bulb on the end of a 1·5 to 2 cm. glass tube, seal up the contents (50 grams of amorphous tellurium and 112 grams of methyl iodide is a convenient amount), and keep in a water-bath at 80° for thirty-six to forty-eight hours. Very little pressure is developed at any time, and none will be found when the cold tube is opened. This is now broken into a mortar, the brittle, red mass finely powdered and extracted with chloroform, and if the same chloroform is used for repeated extractions, very little is necessary. A hot funnel will be required when filtering off the unchanged tellurium. The interaction between methyl iodide and tellurium is very rapid at first, but gradually becomes slow, and eventually appears to stop altogether, even on prolonged heating. In one experiment, when

50 grams of tellurium and 112 grams of methyl iodide were kept at 80° for forty-eight hours, a yield (the yields are calculated on the crystalline iodide obtained from chloroform) of 50 per cent. was obtained.

Precisely the same quantities, when kept at 80° for three weeks, gave only a 55 *per cent. yield.* The *yields are proportionally* greater when small quantities are used.

The α-iodide crystallises from solvents in varying shades of red and *melts and decomposes at* 127°:

0·2293 gave 0·0490 CO_2 and 0·0325 H_2O. C = 5·83; H = 1·57.

0·1890 in 34·65 benzene gave $\Delta t = -0{\cdot}068°$. M.W. = 401.

$C_2H_6I_2Te$ requires C = 5·83; H = 1·46 per cent. M.W. = 411.

The reaction between tellurium and methyl iodide is a reversible *one*,

$$Te + 2CH_3I \underset{100°}{\overset{80°}{\rightleftarrows}} (CH_3)_2TeI_2,$$

proceeding from left to right at 80° and from right to left at or above 100°. In order to show this, a weighed quantity of the iodide was placed in a small bulb blown at the end of a 4 mm. tube, the open end being drawn out into a fine capillary tube and bent at right angles. This constituted a small distilling flask, and the iodide when carefully heated to 100° in a sulphuric acid bath began to decompose. The temperature was gradually raised to 180°, and the distillate collected in a weighed tube kept in ice:

1·2912 gave Te (residue) = 0·4206; CH_3I (distillate) = 0·8352. Te = 32; CH_3I = 65.

$C_2H_6I_2Te$ requires Te = 31; CH_3I = 69 per cent.

These figures are not in close agreement, but are sufficient to show that methyl iodide is the product of decomposition, and not dimethyl telluride. The distillate, also, was quite free from the overpowering odour of the telluride.

The α-iodide is soluble in most organic solvents, the best being chloroform and benzene. To obtain good crystals, boiling saturated solutions should be allowed to cool, and, when cold, the solvent at once decanted, otherwise polymerisation sets in.

The α-iodide is not soluble in cold water, but on prolonged boiling an orange-red solution is obtained which, on cooling, deposits the iodide, leaving a perfectly colourless solution. The salt is partly hydrolysed and the reaction is reversible.

$$TeMe_2I_2 + 2H_2O \rightleftarrows TeMe_2(OH)_2 + 2HI$$

A curious state of equilibrium between the α-base and hydriodic acid results when a boiling saturated solution of the iodide is

suddenly poured into a large excess of cold water. A fine, yellow precipitate at once forms and as quickly disappears, the aqueous solution remaining quite colourless. The base is now in equilibrium with the hydriodic acid, and will remain so indefinitely.

If this perfectly colourless solution is evaporated, crystals of the iodide appear. If hydriodic acid is added, the iodide is at once precipitated.

The action of alkalis and of both aqueous and dry ammonia on the iodide will be dealt with in a separate paper.

A remarkable reaction, which is almost unique, is that between the iodide and mercury diphenyl. If boiling chloroform solutions of the two compounds are suddenly mixed, the mixture will remain perfectly clear and quiescent for a few seconds (this period depending on the concentration of the solutions and on the temperature, decreasing with an increase of concentration and inversely), and then, in a flash, the reaction sets in, and the perfectly clear solution instantly becomes opaque.

The explanation for this reaction probably lies in the formation of an oil (an excessively unstable form of the mercury compound), which is, moreover, very readily soluble in chloroform. At a given moment this oil suddenly changes into the more stable crystalline form, which is quite insoluble in chloroform. Experiment shows the existence of such an oil, and the complete insolubility of the crystalline mercury compound in chloroform rather confirms this hypothesis.

This mercury diphenyl reaction is very characteristic of the α-iodide, and although similar compounds are formed with other aliphatic tellurium derivatives, such as with diethyltelluronium di-iodide (a lemon-yellow salt), the reaction does not take place in this curious manner.

Fuming or concentrated nitric acid precipitates the iodine from the α-iodide, and if the mixture is evaporated on the water-bath the iodine is gradually expelled, and the colourless solution deposits white crystals of the *α-nitrate*, which melts sharply and without decomposition at 142°. This nitrate is explosive when suddenly heated. The α-iodide gives a green platinum salt with chloroplatinic acid.

The α-Base.

This is obtained from the α-iodide by the action of silver hydroxide. Thirty-six grams of silver nitrate and 10 grams of sodium hydroxide are each dissolved in 500 c.c. of water, and the boiling solutions mixed. The mixture is vigorously boiled until the silver

hydroxide becomes granular, when it is collected and washed with 5 litres of boiling water.

Twenty-four grams of the iodide are now ground in a mortar with the freshly prepared silver hydroxide, and sufficient water to make a thin paste. When the red crystals have completely disappeared, the reaction is completed, but it is preferable to allow half an hour to elapse, with occasional grinding, before filtering. The reason of this is that a crystal of the iodide is very liable to become coated with silver iodide, thus impeding further action; hence thorough grinding is necessary.

The silver iodide and mortar are now washed with boiling water, and the filtrate (150—200 c.c.), which is generally somewhat opalescent, contains the α-base. The quantities indicated in this preparation allow for an excess of silver hydroxide.

This strongly alkaline solution behaves in a very similar manner to the mineral bases, and with silver nitrate gives silver hydroxide, probably according to the equation

$$2AgNO_3 + TeMe_2(OH)_2 = 2AgOH + TeMe_2(NO_3)_2.$$

With halogen acids, the α-haloid series results, and undoubtedly a great number of α-derivatives could be prepared with both mineral and organic acids.

The standard method of preparing these α-salts is not by the action of the acid on the base, involving the preparation of the base from the iodide, but the direct interaction between the iodide and the silver salt of the acid, according to the general equation

$$TeMe_2I_2 + 2AgR = TeMe_2R_2 + 2AgI.$$

In this manner, the *benzoate*, which crystallises in white needles melting at 154°, and the yellow *picrate*, crystallising in fine plates, were prepared.

The β-Base.

To prepare the β-base, the α-base is evaporated at 100° under about 15 mm. pressure to complete dryness. The reaction can be closely followed by taking samples and testing with silver nitrate. The point at which the transition from the α- to the β-base is just about to take place is reached when the violent ebullition ceases and an oily liquid remains in the evaporating flask. A sample of this oil, dissolved in water, still shows the presence of the α-base with silver nitrate. If, however, the evaporation is continued for a few minutes longer, this oil, which has momentarily remained perfectly quiescent, will suddenly begin to bubble violently, apparently giving off water, and a white, leaf-like, crystalline substance which adheres to the side of the evaporating flask is obtained. This is the β-base. Due to the sparing solu-

bility of silver hydroxide in water, the base is invariably more or less coloured, the shade varying from pale to dark brown.

To obtain the colourless β-base, it is only necessary to redissolve the discoloured preparation in water, filter, and evaporate again to dryness. This operation can be repeated if necessary.

From 24 grams of the iodide, 6—7 grams of the base are usually obtained, this representing a yield of about 70 per cent. of the theoretical calculated from the equation

$$TeMe_2I_2 + 2AgOH = TeMe_2O + 2AgI + H_2O.$$

Owing to its extremely hygroscopic nature and the difficulty of thoroughly drying this base, a combustion gave but little information as to its constitution:

0·3488 gave 0·1610 CO_2 and 0·1041 H_2O. C = 12·58; H = 3·31.
$C_2H_8O_2Te$ requires C = 12·54; H = 4·18. C_2H_6OTe requires C = 13·83; H = 3·46 per cent.

As will be observed, the value obtained for carbon would indicate a dimethyltelluronium dihydroxide, but that obtained for hydrogen approaches more nearly to dimethyltelluronium oxide.

A certain amount of evidence tends to show that the β-base is dimethyltelluronium oxide, namely, its molecular weight in water, and analysis of the silver salt obtained by treating the base with silver nitrate:

0·5990 in 47·75 water gave $\Delta t = -0·143°$. M.W. = 163. The hydroxide requires M.W. = 192, and the oxide M.W. = 173.*

Analysis of the extremely unstable silver salt gave:

0·2814 gave 0·0403 CO_2 and 0·0305 H_2O. C = 3·91; H = 1·20.
0·1952 „ 0·1088 AgCl. Ag = 41·95.†
$C_2H_6OTe,2AgNO_3$ requires C = 4·66; H = 1·17; Ag = 42·00 per cent.

These figures would therefore point to the existence of a dimethyltelluronium oxide, giving additive products with metallic salts, such as silver nitrate, ferric chloride, etc.

It would therefore not be surprising if similar additive compounds of the general type, $TeMe_2O,2HX$, were formed with halogen acids, these constituting the β-series. Analysis alone is sufficient to refute this hypothesis.

Consideration of the analytical figures for the six haloids unquestionably shows that, whatever the constitution of the β-base may be, a salt results when it is treated with halogen acids, which must correspond in percentage composition and molecular weight

* Two other values were 175 and 183.

† Other values for Ag were 41·90 and 42·00.

with the formula $TeMe_2X_2$, and in consequence the β-base must either have a similar constitution or at least a constitution that lends itself to the formation of such derivatives.

This base also possesses alkaline properties, has a powerful odour, is very hygroscopic, and is readily soluble in both water and alcohol.

With halogen acids, the β-series results, and probably a great number of β-salts, both of inorganic and organic acids, could be prepared.

As previously remarked, the transition from the α- to the β-base readily occurs, but all attempts to obtain the reverse reaction have completely failed.

Prolonged boiling, as well as repeated evaporations to dryness, of an aqueous solution of the β-base, etc., have not produced the slightest change. That the β-form is the most stable of the two is unquestionably the case.

The β-Iodide (β-Dimethyltelluronium Di-iodide).

This iodide is prepared by the action of hydriodic acid on the β-base. This, obtained as previously described from 24 grams of the α-iodide, is dissolved in about 100 c.c. of water, and the acid (D 1·5) is run into it from a burette, the solution being contained in a mortar. A few c.c. are run in at first, and a black, viscid, tarry mass is at once formed which, on trituration, becomes very brittle, and can be finely powdered. This operation is repeated until further addition of hydriodic acid (about 17 c.c. are required) no longer produces a precipitate. This fine, purple powder, which is very heavy, settles rapidly, and the clear, supernatant liquid can be poured off. The crude iodide is collected and kept in a vacuum desiccator over calcium chloride and sodium hydroxide.

The dry salt is now dissolved in a minimum quantity of methyl alcohol, and the solution filtered through a hot funnel. The deep blood-red solution should immediately deposit crystals, and, when cold, these should be collected at once. The crystals can be re-crystallised from methyl alcohol. It also appears to be advantageous to add one or two drops of hydriodic acid to the solvent. A point to be noted is that it is useless to evaporate mother liquors containing the β-iodide, as not only polymerisation, but partial decomposition, with precipitation of tellurium, takes place.

The crystals of the β-iodide vary somewhat in colour, being at times nearly black and at others of an iridescent green. The yields

are necessarily low, on account of loss during crystallisation, but 4 or 5 grams can usually be obtained:

0·8538 gave 0·1828 CO_2 and 0·1168 H_2O. C=5·84; H=1·52.
0·3138 „ 0·3578 AgI. I=61·62.
0·4482 in 32·55 acetone gave E=0·046°. M.W.=509.
$C_2H_6I_2Te$ requires C=5·83; H=1·46; I=61·72 per cent.
M.W.=411.*

The α-Bromide (α-Dimethyltelluronium Dibromide).

The α-bromide can be prepared by the action of hydrobromic acid on the α-base. The solution of α-base, prepared as described from 24 grams of the α-iodide, usually has a volume of between 150 and 200 c.c., and should be evaporated to about 100 c.c. The acid (D 1·3) is now run in from a burette until no further precipitation takes place. The crude bromide is collected and crystallised from ethyl or methyl alcohol. A pure salt is at once obtained, and, after thoroughly drying over calcium chloride and sodium hydroxide, the leaf-like crystals melt at 92°. Unless the preparation is entirely freed from acid by drying over sodium hydroxide, the melting point will invariably be low.

A more direct method consists in dissolving the α-iodide in aqueous ammonia, precipitating the iodine with an ammoniacal solution of silver nitrate, and treating the dimethyltelluronium dinitrate with hydrobromic acid.

This reaction is very complicated, but can be summarised by the equations:

(1) $TeMe_2I_2 + 2AgNO_3 = TeMe_2(NO_3)_2 + 2AgI$,
(2) $TeMe_2(NO_3)_2 + 2HBr = TeMe_2Br_2 + 2HNO_3$.

Concentrated aqueous ammonia is run drop by drop from a burette on 15 grams of the α-iodide (an exothermic reaction) until the red salt is completely transformed into a pasty, greyish-white mass. This will need but a few c.c., and it is advisable to stir thoroughly during the reaction, as the greyish-white precipitate has a tendency to cake, thus preventing further action of the ammonia. This precipitate is now dissolved in about 200 c.c. of water with a drop or two of ammonia if any of the undecomposed

* Another determination gave M.W.=707. These values are high, owing to polymerisation of the salt in the solvent. Experiment has shown that: (1) the molecular weight increases regularly with the concentration, and (2) the molecular weight is higher in boiling acetone than it is in freezing nitrobenzene, for the same concentration. This polymerisation is more marked in the case of the β-iodide than it is with the β-bromide. The β-chloride shows no sign of polymerisation and correct values are obtained.

iodide is observed. Fifty c.c. of an aqueous solution containing 12·4 grams of silver nitrate, with just sufficient ammonia to redissolve the precipitate of silver hydroxide, are now added, and the mixture is boiled and filtered. The filtrate is evaporated on a water-bath until the odour of ammonia has completely disappeared, diluted again to 200 c.c., and any silver iodide removed by filtration.

A drop of hydrobromic acid is added to the boiling solution, and if a yellow, insoluble precipitate forms, this indicates an excess of silver nitrate. In this case, a further addition of acid is necessary. Any silver bromide is now filtered off, and the solution evaporated to about 100 c.c.

The cold filtrate is treated with acid (hydrochloric or hydrobromic, according as to whether the α-chloride or α-bromide is desired) until no further precipitation takes place. The crude salt can now be crystallised from ethyl or methyl alcohol. The yields are good, and about 5 or 6 grams are usually obtained after a second crystallisation from alcohol:

0·7248 gave 0·2004 CO_2 and 0·1246 H_2O. C = 7·54; H = 1·91.
0·3350 „ 0·3956 AgBr. Br = 50·25.
0·6512 in 31·42 acetone gave E = 0·105°. M.W. = 335.
$C_2H_6Br_2Te$ requires C = 7·56; H = 1·89; Br = 50·39 per cent.
M.W. = 317.

The β-Bromide (β-Dimethyltelluronium Dibromide).

The β-base from 24 grams of the α-iodide is diluted to about 150 c.c., and hydrobromic acid (D 1·3) is run in from a burette (25—35 c.c. of acid are generally required).

So long as an excess of base is present, the white, gelatinous precipitate redissolves. On continued addition of acid, a somewhat granular, insoluble precipitate separates which, on further treatment, becomes bright orange and crystalline. This is the bromide, which can be recrystallised from ethyl alcohol, etc.

In this preparation, mother liquors containing a little free acid can be evaporated on a water-bath and allowed to crystallise.

A certain amount of tellurium, due to slight reduction, is liable to precipitate on treatment of the base with the acid, and this is especially the case when a too concentrated solution of the base is used. The crude bromide is therefore liable to be more or less discoloured.

It is also not advisable to have a marked excess of acid, as this appears to react further with the β-bromide, giving a brown,

additive compound. The yields are good, and 6 or 7 grams of the crude bromide can usually be obtained.

The leaf-like crystals, or bright orange, crystalline powder, darken at about 135° and melt and decompose at about 142°. Repeated crystallisations of this bromide do not alter the melting point:

0·6944 gave 0·1914 CO_2 and 0·1206 H_2O. C = 7·52; H = 1·93.
0·3564 ,, 0·4218 AgBr. Br = 50·36.
0·3034 in 46·61 nitrobenzene gave $\Delta^t = -0·123°$. M.W. = 370.
$C_2H_6Br_2Te$ requires C = 7·56; H = 1·89; Br = 50·39 per cent.
M.W. = 317.*

The α-Chloride (α-Dimethyltelluronium Dichloride).

This is prepared in exactly the same manner as the α-bromide, both by the action of hydrochloric acid on the base or directly from the α-iodide. It is the most stable of all the dimethyltelluronium dihaloids, does not appreciably polymerise, and can be crystallised from water, alcohol, etc. From concentrated solutions leaf-like crystals deposit, and from dilute aqueous solutions long needles, with the same melting point of 92°, are obtained:

0·5693 gave 0·2196 CO_2 and 0·1340 H_2O. C = 10·52; H = 2·62.
0·3618 ,, 0·4560 AgCl. Cl = 31·17.
0·2224 in 19·38 acetone gave $E = 0·085°$. M.W. = 229.
$C_2H_6Cl_2Te$ requires C = 10·50; H = 2·62; Cl = 31·05 per cent.
M.W. = 228.

The β-Chloride (β-Dimethyltelluronium Dichloride).

To prepare this chloride, the directions given for the preparation of the β-bromide are followed. The precipitation of tellurium when hydrochloric acts on the base is not quite so marked as with the β-bromide, but the crude chloride is generally somewhat discoloured. The leaf-like crystals melt sharply at 134°:

0·3496 gave 0·1346 CO_2 and 0·0830 H_2O. C = 10·50; H = 2·64.
0·2206 ,, 0·2777 AgCl. Cl = 31·11.
0·1648 in 19·11 acetone gave $E = 0·065°$. M.W. = 226.†
$C_2H_6Cl_2Te$ requires C = 10·50; H = 2·62; Cl = 31·05 per cent.
M.W. = 228.

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* Other values obtained for the molecular weight were: 400, 445 (nitrobenzene), 430, 459, 525 (acetone).

† Other values found were 230 : 223 (acetone).

XIV.—*The Action of Aqua Regia on Gold–Silver Alloys in the Presence of Ammonium Salts.*

By WILLIAM BRANCH POLLARD.

THE most practical method of dissolving gold and its alloys is undoubtedly by means of aqua regia.

With gold alloys containing upwards of 15 per cent. of silver, a coating of silver chloride forms on the surface of the metal and protects it from the further action of the acid.

By rolling out these alloys until they are very thin, solution can often be effected, the coating on the metal never becoming sufficiently thick to stop the reaction; thicker pieces are only superficially attacked.

With alloys which are very rich in silver, "rolling out" is not sufficient to effect solution, and a black coating forms and resists all further action of the acid.

In order to study the matter further, the following alloys were prepared, the composition being stated in parts per thousand:

Au.	Ag.	Cu.
625	375	—
500	500	—
333	667	—
250	750	—
453	277	270

The alloys were rolled out to about a tenth of a millimetre in thickness, and portions of them were used in the subsequent tests.

It seemed probable that the best way to effect solution of these alloys would be to try and increase the solubility of the silver chloride in the liquid; of the various chlorides which are known to dissolve silver chloride, ammonium chloride appeared to be the most promising for this purpose.

To test the point, a gram of each of the above-mentioned alloys was placed into a bottle, aqua regia (containing one part of concentrated nitric acid and three parts of concentrated hydrochloric acid) added, and the bottle placed on a hot asbestos board. The action of the acid started almost immediately, but stopped very quickly, the surface of the metal being covered with a black coating. Ammonium chloride was now added to the hot liquid as long as it was dissolved. In a very short time, the black coating on the metal had completely dissolved, leaving a bright, metallic surface in each case. The acid now began to attack the metal

again, and continued to do so until all had dissolved; no silver chloride separated, and a clear, yellow solution was obtained. On diluting the solutions with water, copious precipitates of perfectly white silver chloride separated. Even pure silver was found to be soluble in a mixture of aqua regia and ammonium chloride, although the action was not very rapid and the volume of liquid required was large in comparison with the amount of metal dissolved. It is to be noted that aqua fortis and sal-ammoniac were used by the alchemists for dissolving gold. It seems most probable that this mixture was used to dissolve native gold, which sometimes contains enough silver to prevent dissolution in aqua regia alone.

The chief objection to the use of aqua regia and ammonium chloride seemed to be that the action of the acid was very slow, and when much silver was present the volume of the solution became large.

It was noticed that the alloy containing gold 453, silver 277, and copper 270 dissolved very easily in a mixture of aqua regia and ammonium nitrate, the silver chloride remaining insoluble.

Alloys of gold and silver only did not dissolve so easily in this mixture, but when ammonium chloride was added as well, a most marked improvement took place.

For most alloys, a mixture of 5 grams of ammonium chloride, 5 grams of ammonium nitrate, and 5 to 10 c.c. of aqua regia was found to give quite satisfactory results.

The amount of metal which can be dissolved depends on the amount of silver present. If silver chloride separates, this shows that enough ammonium chloride has not been added. If, on the other hand, the action becomes slow, more aqua regia may be required.

With 5 grams of each salt and 5 to 10 c.c. of aqua regia, 0·5 to 1 gram of alloy could be dissolved easily and quickly, the total volume of the solution being quite small.

Considerably more gas is evolved when gold dissolves in the presence of ammonium salts than when it is dissolved in aqua regia alone; on collecting the gas, it appeared to consist principally of nitrogen. The solution of the gold, therefore, does not take place in accordance with Priwoznik's equation (*Oesterr. Zeitsch. Berg.- u. Hüttenw.*, 1910, **58**, 549), a secondary action occurring whereby the ammonium salts become oxidised with evolution of nitrogen.

During the attack of gold–silver alloys by aqua regia in the presence of ammonium chloride and nitrate, it often happened

that purplish-brown crystals separated in the liquid. When water was added, they disappeared, and nothing remained but silver chloride. A specially good yield of these crystals was obtained when 2 grams of an alloy of the composition Au 625, Ag 375 were treated with a mixture consisting of 10 grams of ammonium chloride, 3 grams of ammonium nitrate, 5 c.c. of concentrated nitric acid, and 15 c.c. of concentrated hydrochloric acid. The alloy, in the form of thin sheet, was heated gently in a beaker with the above mixture. When all the metal was dissolved, the bottom of the beaker was found to be covered with very small, purplish-brown crystals. They were instantly decomposed by water, with the formation of silver chloride and chloroauric acid, but were found to be fairly stable in concentrated hydrochloric acid.

When prepared in this way, it was found difficult to prevent the crystals being contaminated with ammonium chloride. The following method was therefore devised.

Preparation of the Salt.—Twenty-five grams of gold were dissolved in 50 c.c. of nitric acid and 150 c.c. of hydrochloric acid, the liquid being then saturated with about 30—35 grams of ammonium chloride. Three grams of silver nitrate dissolved in 10 c.c. of water were then added, and a copious precipitate of silver chloride formed in the liquid. On adding a few crystals of ammonium chloride, the silver chloride began at once to change into brown crystals. On heating the liquid, the crystals were converted into silver chloride, and, on cooling, again reappeared. This change could be repeated any number of times.

The crystals were allowed to remain in contact with the mother liquor for two or three days to ensure all the silver chloride being converted into the brown salt. The mother liquor was then poured off, saturated with ammonium chloride, and a further amount of silver nitrate added to the solution. A second crop of crystals resulted, and these were heated and allowed to cool as before. The formation of the salt in a hot solution gives rise to larger and better formed crystals than when the preparation is made in a cold solution.

The process was then again repeated, four preparations in all being obtained before the gold became exhausted in the mother liquor. The crystals were freed from the mother liquor in a centrifuge, and afterwards dried at 100°. They were then placed in a Soxhlet thimble and extracted with ether (distilled from sodium) until ... They were afterwards heated at 15... , and the remaining

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traces of ammonium chloride sublimed away. A second treatment with ether followed, after which the crystals were dried and analysed.

Found: Ag = 15·58; Au = 37·99; NH_4 = 6·88; Cl = 39·44.
$3AgCl,4AuCl_3,8NH_4Cl$ requires Ag = 15·62; Au = 38·06; NH_4 = 6·97; Cl = 39·35 per cent.

Crystallographic Examination.

The crystallographic examination was made by Miss I. E. Knaggs in the Mineralogical Laboratory of the University of Cambridge under the direction of Dr. A. Hutchinson, for whose help and assistance the author wishes to express his gratitude.

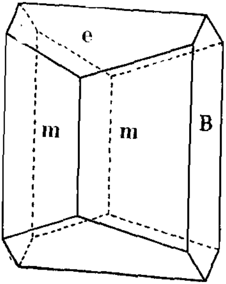
Crystal System.—Orthorhombic.

Class.—Holohedral.

Axial Ratio.—$a:b:c = 0·5376:1:0·3210$.

Forms Observed.—*B*(010), *m*(110), *e*(101).

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.
mB = (010) : (1$\bar{1}$0)......	4	61°43′—61°45′	61°44′	61°44′
mm‴ = (110) : (1$\bar{1}$0)......	7	56°28′—56°35′	56°32′	—
me = (110) : (101)......	5	63°10′—63°11′	63°10½′	—
ee′ = (101) : ($\bar{1}$01)......	3	61°39′—61°45′	61°42′	61°41′



Habit.—The crystals available for measurement consisted of minute prisms sometimes modified by the brachypinakoid (010), and terminated at either end by the macrodome (101). Some of the preparations consisted of larger crystals showing (110) and

(010) in approximately equal development. These had rough ends and were not suited for accurate measurement.

Cleavage.—None observed.

Optical Characters.—The crystals were very dark red by reflected light, and owing to their intense absorption it was difficult to make determinations of their optical characters. Some of the smallest and thinnest prisms when mounted so that light traversed them along the *Y* axis were found to be strongly pleochroic, absorption being almost complete for rays vibrating parallel to the axis of *Z*, whilst red light was transmitted fairly freely by vibrations parallel to the axis of *X*. When the crystal was rotated so that light traversed it along the *X* axis, strong absorption was observed of the ray vibrating parallel to *Y* as well as of that vibrating parallel to *Z*. No characteristic interference figure could be observed in convergent light, nor was it possible to determine the refractive indices either by the prism methods or by total reflection. By the immersion method they were found to be high —greater than 1·74.

GOVERNMENT LABORATORY,
CAIRO. [*Received, October 17th*, 1919.]

XV.—*Intramolecular Rearrangement of the Alkylarylamines: Formation of 4-Amino-n-butylbenzene.*

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

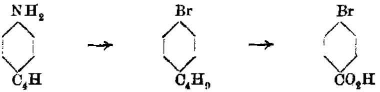
AN important reaction of many of the *N*-substitution products of the arylamines is their rearrangement to *C*-substitution compounds. This change occurs with the majority of the common substituent groups, such as halogen, nitro-, nitroso-, sulphonyl, and alkyl. The intramolecular change of the chloroarylamines may be explained in terms of the variable valency of the nitrogen atom (compare Blanksma, *Rec. trav. chim.*, 1903, **22**, 290; Orton and Jones, *Rep. Brit. Assoc.*, 1910). The formation of *p*-chloroacetanilide from *N*-chloroacetanilide is accompanied by the formation of an additive compound (compare Armstrong, T., 1900, **77**, 1051). The presence of a catalyst is necessary in many molecular changes involving the migration of a nitroso- or nitro-group, as in the production of *p*-nitrosoalkylanilines from nitrosoamines and of nitroanilines from nitroamines. Whilst the bromo- and chloro-aniline derivatives have been thoroughly investigated, as well as the nitroso- and sulphonyl

substituted alkylanilines, the intramolecular change of the alkylarylamines has not been dealt with in such detail.

The earlier work in the production of aminoalkylbenzenes showed that they could be formed either by heating (*a*) aniline hydrochloride and the alcohol, or (*b*) the alkylaniline hydrochloride, at temperatures above 300° (compare Hofmann, *Ber.*, 1872, **5**, 729). Since methylaniline hydrochloride on heating in a current of hydrogen chloride yields methyl chloride, it has been generally assumed that a somewhat similar reaction would occur in an autoclave or sealed tube on heating the alkylaniline hydrochloride.

On heating *n*-butylaniline hydrochloride in a sealed tube, amino-*n*-butylbenzene was the main product. In addition, ammonia, aniline, and 4-butylamino-*n*-butylbenzene were formed, together with smaller amounts of more highly butylated products. There was also obtained a portion soluble in concentrated hydrochloric acid, and precipitated on dilution, which probably contained diphenylamine derivatives. In addition to the hydrochloride, the alkylaniline zincichloride and certain other compounds with metallic salts also undergo this transformation on heating. The chief product resulting from the intramolecular rearrangement of *n*-butylaniline is, however, 4-amino-*n*-butylbenzene. To explain the formation of this compound from *n*-butylaniline it might be supposed that the latter decomposes partly to aniline and *n*-butyl chloride or butylene; either of the last two might then be supposed to react with aniline. The production of *n*-butyl chloride is probably excluded in the case where zinc chloride replaces the hydrochloric acid. By heating *n*-butylaniline hydrochloride in a sealed tube or in an open flask, a small amount of a gas is obtained, which resembles butylene in being unsaturated. It appears possible that butylene may result as an intermediate product in the change. By heating *n*-butylaniline hydrochloride under atmospheric pressure a certain amount of 4-aminobutylbenzene is produced. If butylene is formed as an intermediate product, some *sec.*-butylbenzene should be obtained. An examination of the end-products shows that amino-*sec.*-butylbenzene is present, generally, at the most, only in traces.

The orientation of aminobutylbenzene (I), obtained by the intramolecular rearrangement of *n*-butylaniline, was determined by con-



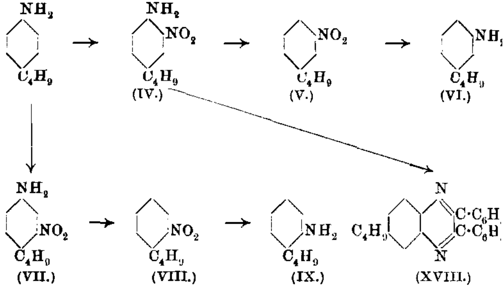
(I.) (II.) (III.)

verting the purified amino-derivative into bromobutylbenzene (II), which, on oxidation with chromic acid, gave *p*-bromobenzoic acid (III).

It cannot be assumed with certainty that *n*-butyl alcohol and aniline zincichloride will yield a compound containing a *n*-butyl group. An examination of the literature shows that a rearrangement of the alkyl group often occurs when it is introduced into the benzeue ring. The rearrangement of the *n*-butyl chloride and *iso*butyl chloride in the formation of butylbenzenes by the Friedel and Crafts reaction is well established. The rearrangement of alkyl groups in the formation of aminoalkylbenzenes also appears to take place. Effront (*Ber.*, 1884, **17**, 2324), by the action of *iso*butyl alcohol on *o*-toluidine hydrochloride, obtained 5-*tert*.-butyl-*o*-toluidine, which by the diazo-reaction yielded a phenol identical with that obtained by heating *tert*.-butyl chloride, *o*-cresol, and zinc chloride (compare Baur, *Ber.*, 1894, **27**, 1615). It is also probable that by the action of *iso*butyl alcohol on aniline hydrochloride amino-*tert*.-butylbenzene is obtained. The recorded physical constants of the derivatives of 4-amino*iso*butylbenzene and 4-*amino-tert*.-butylbenzene are practically identical, and doubt must be thrown on their existence as two compounds (compare Studer, *Annalen*, 1882, **211**, 234; Senkowski, *Ber.*, 1890, **23**, 2412; Malherbe, *Ber.*, 1919, **52**, [*B*], 319).

It became necessary, therefore, to determine the configuration of the butyl group of the primary amine from *n*-butyl alcohol and aniline. By heating aniline zincichloride with *sec*.-butyl alcohol an amine was obtained, boiling at 240°, or 20° lower than that obtained from the normal alcohol, and yielding a different series of derivatives. As there was only a small quantity of this amine available it was not possible to determine the orientation of the butyl groups. Any doubt that the primary amine from *n*-butyl alcohol boiling at 258° was not a normal derivative was removed by preparing from it the other two monoamino-compounds. A comparison of the derivatives of the amines thus prepared shows that the amine from *sec*.-butyl alcohol differs from the one from *n*-butyl alcohol in the configuration of the butyl group.

By the nitration of 4-*acetylamino*-n-*butylbenzene*, followed by hydrolysis, 3-*nitro*-4-*amino*-n-*butylbenzene* (IV) was obtained as a red solid of low melting point. The orientation of the nitro-group was determined by converting the compound into a diamine, which condensed with benzil to yield 2:3-*diphenyl*-6-n-*butylquinoxaline* (XVIII). On eliminating the amino-group from 3-nitro-4-aminobutylbenzene, 3-*nitro*-n-*butylbenzene* (V) was obtained as a pale yellow oil boiling at 275—277°.

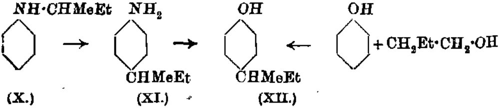


Nitration of 4-amino-*n*-butylbenzene in the presence of sulphuric acid gave *2-nitro-4-amino-n-butylbenzene* (VII), melting at 52° which by the diazo-reaction yielded *2-nitro-n-butylbenzene* (VIII), a yellow oil distilling with some decomposition. Reduction of 2-nitro and 3-nitro-*n*-butylbenzenes gave primary amines, the derivatives of which are distinct from those obtained from the primary amine boiling at 240° from *sec.*-butyl alcohol. It must be concluded therefore, that in the intramolecular transformation of *n*-butyl aniline 4-amino-*n*-butylbenzene is obtained.

The following table shows clearly the difference between the amines obtained:

	Acetyl compound, m. p.	Benzoyl compound, m. p.
2-Amino-*n*-butylbenzene	100°	—
3-Amino-*n*-butylbenzene	Not obtained crystalline.	68°
4-Amino-*n*-butylbenzene	*105°*	*126°*
4-Amino-*sec.*-butylbenzene ...	126°	—

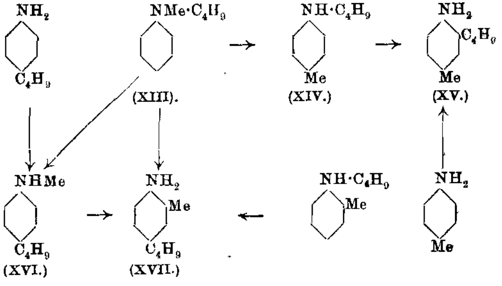
Although *n*-butyl alcohol reacts with aniline zincichloride to yield 4-amino-*n*-butylbenzene, it gives with phenol, in the presence of zinc chloride, hydroxy-*sec.*-butylbenzene. The constitution of the latter compound was shown by its identity with the hydroxy-derivative obtained from 4-amino-*sec.*-butylbenzene (XI) by the aid of the diazo-reaction.



It has been shown by Mailhe and Godon (*Compt. rend.*, 1918, **166**, 467) that methylaniline and methyltoluidine are stable at moderately high temperatures, as they may be produced by passing a mixture of methyl alcohol and the primary arylamine over a suitable catalyst heated to 400°. No intramolecular rearrangement is observed when methyl- or ethyl-aniline is passed over heated nickel; instead, a decomposition into aniline and methane or ethylene occurs (Sabatier and Gaudion, *Compt. rend.*, 1917, **165**, 309). It has been found that *n*-butylaniline may be heated for several hours at 240—260° without the production of any amino-butylbenzene. Furthermore, the addition of substances which show no tendency to combine with butylaniline, such as calcium sulphate, sodium chloride, or silica, does not bring about any migration of the alkyl group to the nucleus. The formation of 4-amino-*n*-butylbenzene from *n*-butylaniline has been observed to take place only when a substance is added which combines with butylaniline. Substances such as hydrochloric acid, zinc chloride, cobalt chloride, and cadmium chloride have been chiefly employed, and with all these salts the additive compounds have been isolated. It appears that for intramolecular rearrangement of the alkylarylamines to occur, the presence of a substance which is capable of uniting with the amino-group is necessary.

The rearrangement of *n*-butylaniline cannot be satisfactorily explained by assuming the intermediate formation of either butyl chloride or butylene. Orton (*loc. cit.*) has suggested that amino-benzenes and their *N*-substituted derivatives are capable of existing as dynamic isomerides. It is possible that the transference of the alkyl group to the nucleus might occur during one of these phases. To attempt to explain the intramolecular rearrangement of alkyl-arylamines, the alkyl groups attached to the aminic nitrogen are assumed tentatively to exist in a state of oscillation, following a system of vibration which is definite as long as the external conditions remain constant. The calling into play of the residual valency of the nitrogen atom will have the effect of introducing more groups round the nitrogen atom, with the result that a rearrangement of the alkyl groups may occur. The disturbing effect will depend on several factors, such as the space occupied by each group, its vibration path, and also the polarity of the group. The groups already attached to the nitrogen will have the effect of hindering the entry of another group, corresponding with the space occupied by them. They will also tend to be displaced farther away from the nitrogen atom according to the hindrance produced by them, and there will be a tendency for the alkyl groups to be removed in the order of their steric relations to one another.

Experiments were carried out in order to measure the relative ease with which differing alkyl groups were expelled from the alkylanilines. The earlier measurements were made by heating the monomethyl- and monobutyl-anilines separately in sealed tubes under similar conditions, so far as possible, with various substances. The results indicate that *n*-butylaniline undergoes intramolecular change the more readily, but the method is open to several objections. It was impossible to ensure absolutely identical conditions for each substance, such as the same temperature and pressure inside each tube. It is also likely that in the formation of the additive compounds of the alkylanilines, steric effects may have an influence, so that the rearrangement caused in the molecule may be counterbalanced to some extent by the steric hindrance due to the alkyl group. To overcome these probable sources of error the intramolecular rearrangement of dissimilarly substituted tertiary alkylanilines has been investigated. Methyl-*n*-butylaniline (XIII) was heated in a sealed tube in the presence of hydrogen chloride, zinc chloride, or cobalt chloride. The products of the rearrangement should then indicate whether the larger alkyl groups are the more readily removed. Thus methyl-*n*-butylaniline should yield as a first step methylaminobutylbenzene (XVI) or butyltoluidine (XIV), according to whether the butyl or the methyl group is the more mobile.



The constitution of the product was determined by dissolving the mixture of amines in dilute hydrochloric acid and adding in slight excess a solution of sodium nitrite. The secondary amines were removed as nitrosoamines, which could be converted into solid nitro-derivatives. Any diazonium salt in the solution was converted into the corresponding azo-β-naphthol derivative, which

would serve to identify the primary amine originally present. An examination of the products of nitration of the secondary amines resulting from the intramolecular rearrangement of methyl-*n*-butylaniline indicated that a mixture was present, from which 3:5-dinitro-*n*-butyl-*p*-toluidine and 2:4:6-trinitrophenylmethylnitroamine were isolated in small quantities. It has not yet been possible to determine the complete composition of the mixture.

The *azo-β-naphthol* compounds were reduced, yielding the original primary amines present after intramolecular change had taken place. Analytical results showed that these amines were aminomethylbutylbenzenes, although in one case *p*-tolueneazo-β-naphthol was isolated in small amount by recrystallisation of the azo-β-naphthols. It appears, therefore, that in the reaction both the methyl and butyl groups have undergone intramolecular rearrangement, and until a method has been elaborated for determining the composition of the products it is not possible to determine accurately the relative ease with which the different alkyl groups are removed.

The elimination of alkyl groups of alkylanilines on heating in a current of hydrogen chloride was also investigated. The secondary amines present in the mixture were isolated as nitrosoamines, and these were nitrated in glacial acetic acid by means of fuming nitric acid and converted into the corresponding trinitrophenylalkylnitroamines. It was found that methyl-*n*-butylaniline yielded a mixture of secondary amines, and 2:4:6-trinitrophenylmethylnitroamine was isolated from the mixture of nitroamines. The melting point of the nitration product was lower than either that of trinitrophenylmethylnitroamine or the corresponding butyl derivative, and was probably a mixture containing these two compounds.

In experiments on the elimination of alkyl groups from dissimilarly substituted alkylarylamines it is essential to use a pure tertiary amine, unmixed with any secondary amine. The methyl-*n*-butylaniline employed was purified by fractionation, followed by heating it with phenylcarbimide. The boiling point of the amine obtained in this way differed considerably from that recorded by Komatsu (*Mem. Coll. Sci. and Eng. Kyoto Imp. Univ.*, 1912, **3**, 371), who also prepared this amine. He records the boiling point as 225—230°, and states that it yields a picrate melting at 143°. Methyl-*n*-butylaniline, purified in the manner indicated above, boils at 242·5° and yields a picrate melting at 90°. The melting point of the picrate is thus brought into agreement with those of other tertiary butylanilines.

By increasing the size of the alkyl group in alkylbutylanilines the melting point of the picrate is raised. The following table shows

the effect of displacing the methyl group in methylbutylaniline by larger groups.

Methyl-*n*-butylaniline	boils at	242·5°.	The picrate melts at	90°.
Ethyl-*n*-butylaniline	,,	248°.	,, ,, ,,	100°.
Di-*n*-butylaniline	,,	260—263°.	,, ,, ,,	125°.

The nitration of tertiary alkylanilines was also studied. On nitrating methylbutylaniline under vigorous conditions, the principal product is 2:4:6-trinitrophenylmethylnitroamine, showing that the larger group has been eliminated. Meldola and Hollely (T., 1915, **107**, 610) have found that in the nitration of acetylated *as*-dialkylphenylenediamines a similar action occurs, the larger groups being removed in the nitration, in preference to the smaller groups.

On nitrating ethyl-*n*-butylaniline both trinitrophenylethylnitroamine and trinitrophenyl-*n*-butylnitroamine are produced. The difference in the relative proportions of the two products of the nitration appears to be less than in the case of methyl-*n*-butylaniline.

Trinitrophenylmethylnitroamine is also obtained on nitrating dimethylaniline under vigorous conditions. Toward the end of the operation there is the usual vigorous effervescence due to the elimination of the methyl group as carbon dioxide. In nitrating di-*n*-butylaniline under similar conditions there is practically no effervescence, and from the mixture after nitration a volatile fatty acid was isolated, which was identified as *n*-butyric acid by means of its distillation constant.

EXPERIMENTAL.

The Amino-derivative of n-*Butylbenzene: 4-Amino-*n-*butylbenzene.*

In the preparation of 4-amino-*n*-butylbenzene, *n*-butyl alcohol was allowed to react with aniline in the presence of a suitable condensing agent, such as zinc chloride. Approximately molecular quantities of aniline and dry *n*-butyl alcohol were mixed with fused zinc chloride (0·5 mol.), and the mixture was heated in an electrically wound autoclave for twenty-four hours at 230—240°. The product was washed first with water to remove uncombined zinc chloride and finally with ether or light petroleum (b. p. 80—100°). In this way secondary amines and other by-products were removed, leaving behind the zincichlorides of the primary amines, from which a mixture of these amino-compounds was obtained by treatment with warm concentrated sodium hydroxide solution. Fractionation of the mixture of bases yielded 4-amino-*n*-butylbenzene. By using

amounts of zinc chloride less than the molecular proportion—even as low as one-seventh of the amount quoted above—4-amino-*n*-butylbenzene was still produced, but the yield was not so good.

The *hydrochloride* is precipitated on adding an excess of concentrated hydrochloric acid to an aqueous suspension of the base. It is readily soluble in water or alcohol, but only sparingly so in an excess of hydrochloric acid:

0·1063 gave 6·9 c.c. N_2 at 21° and 751 mm. N = 7·5.*
0·1420 „ 0·1093 AgCl. Cl = 19·0.
$C_{10}H_{15}N,HCl$ requires N = 7·5; Cl = 19·1 per cent.

The *hydrobromide* crystallises from aqueous solution containing free hydrobromic acid in large, white plates. It is readily soluble in water or alcohol:

0·0785 gave 0·0654 AgBr. Br = 34·6.
$C_{10}H_{15}N,HBr$ requires Br = 34·7 per cent.

The *sulphate* crystallises from moist ether in a felted mass of white crystals. It is sparingly soluble in water:

0·1002 gave 6·1 c.c. N_2 at 20° and 737 mm. N = 6·9.
0·3502 „ 0·2058 $BaSO_4$. H_2SO_4 = 24·7.
$(C_{10}H_{15}N)_2,H_2SO_4$ requires N = 7·1; H_2SO_4 = 24·7 per cent.

From warm alcohol it separated as a mass of colourless crystals which under the microscope had the appearance of interlaced laths.

The *platinichloride* is a pale brownish-yellow powder, sparingly soluble in water, and more readily so in alcohol. It crystallises from absolute methyl alcohol in small needles melting and decomposing at 200—202°:

0·1203 gave 0·0330 Pt. Pt = 27·4.
$(C_{10}H_{15}N)_2,H_2PtCl_6$ requires Pt = 27·6 per cent.

The *acetyl* derivative, obtained from 4-amino-*n*-butylbenzene by the action of acetic anhydride, crystallises from alcohol in white plates melting at 105°:

0·1426 gave 8·8 c.c. N_2 at 17° and 755 mm. N = 7·3.
$C_{12}H_{17}ON$ requires N = 7·3 per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann reaction, crystallises from alcohol in bulky groups of fine needles melting at 126°:

0·1015 gave 4·65 c.c. N_2 at 17° and 748 mm. N = 5·3.
$C_{17}H_{19}ON$ requires N = 5·5 per cent.

* In the nitrogen estimations recorded in this paper, the gas was measured over 40 per cent. potassium hydroxide solution, and the pressure has been corrected for vapour tension.

α-Phenyl-β-4-n-butylphenylcarbamide, $C_4H_9 \cdot C_6H_4 \cdot NH \cdot CO \cdot NHPh$.

4-Amino-*n*-butylbenzene was treated with a solution of one molecular proportion of phenylcarbimide dissolved in light petroleum (b. p. 60—80°), and after remaining at the ordinary temperature for two or three hours the precipitate was collected, washed several times with small quantities of light petroleum, and dried:

0·1002 gave 0·2790 CO_2 and 0·0678 H_2O. C=75·9; H=7·5.
0·1012 „ 9·1 c.c. N_2 at 20° and 757 mm. N=10·5.
$C_{17}H_{20}ON_2$ requires C=76·1; H=7·5; N=10·4 per cent.

It crystallises from aqueous alcohol in bulky masses of small, white needles melting at 160°. It is soluble in ether, acetone, ethyl acetate, or glacial acetic acid, but sparingly so in water or light petroleum.

4-Bromo-n-butylbenzene.

The orientation of the butyl group was determined by converting the amino-*n*-butylbenzene into a derivative that could yield a substituted benzoic acid by oxidation. For this purpose the amino-group was displaced by bromine by the Sandmeyer reaction. 4-Amino-*n*-butylbenzene was dissolved in three molecular proportions of hydrobromic acid and diazotised by the addition of sodium nitrite solution. On adding a solution of cuprous bromide in hydrobromic acid, followed by distillation in a current of steam, *4-bromo-n-butylbenzene* was obtained as a pale yellow oil of pleasant, ethereal odour, denser than water, and boiling at 242—243°/755 mm.:

0·0853 gave 0·1762 CO_2 and 0·0460 H_2O. C=56·4; H=6·0.
$C_{10}H_{13}Br$ requires C=56·3; H=6·1 per cent.

That the bromo- and alkyl groups are in the para-position follows from the production of *p*-bromobenzoic acid by oxidation. Half a gram was heated in a sealed tube with 12 c.c. of a 6 per cent. solution of chromic acid for seven hours at 150—200°. There was practically no pressure on opening the tube, which contained a green, amorphous mass together with tarry matter and some white, glistening, needle-shaped crystals. The contents of the tube were rendered alkaline, and after removing the suspended matter, a grey solid was precipitated on adding dilute sulphuric acid. It was purified by dissolving in sodium carbonate solution, and any traces of volatile bromo-compounds were removed by means of a current of steam. The addition of dilute hydrochloric acid precipitated a white solid which crystallised from ether in small needles melting at 250°. This melting point is almost identical with that recorded for *p*-bromobenzoic acid (251°), and is considerably higher than those of the other two monobromobenzoic acids.

Diazoamino-4-n-butylbenzene.

The base (1 mol.) was dissolved in glacial acetic acid (3 mols.) and the solution diluted. On adding sodium nitrite solution, a yellow, semi-solid mass separated which quickly became hard. The *diazoamino-4-n-butylbenzene* was collected and, after washing several times with water to remove any traces of nitrous acid, crystallised from light petroleum, from which it separated in masses of slender, sulphur-yellow needles melting at 75°:

0·0743 gave 9·0 c.c. N_2 at 24° and 742·5 mm. N = 13·7.

$C_{20}H_{27}N_3$ requires N = 13·6 per cent.

When exposed to the light it darkened slowly.

4-n-Butylbenzeneazo-β-naphthol.

A solution of the hydrochloride of the base was diazotised and, after removing the excess of nitrous acid by means of carbamide, it was poured into an alkaline solution of β-naphthol. The red *azo*-compound crystallised from hot alcohol in bright red bunches of slender needles melting at 80°:

0·1088 gave 9·8 c.c. N_2 at 15·3° and 741 mm. N = 9·4.

$C_{20}H_{20}ON_2$ requires N = 9·2 per cent.

4-n-Butylbenzeneazo-β-naphthol is insoluble in a 30 per cent. solution of potassium hydroxide. It dissolves in concentrated sulphuric acid with the production of a brilliant purple colour, which gives place to a faint brown coloration on dilution.

4-n-Butylbenzeneazophenyl-β-naphthylamine.

This derivative was prepared by adding a diazotised solution of 4-amino-*n*-butylbenzene, freed from excess of nitrous acid, to one molecular proportion of phenyl-β-naphthylamine dissolved in acetic acid. An excess of sodium acetate was then added, and the red product was allowed to remain at the ordinary temperature for two to three hours, with occasional stirring. Water was added to complete the precipitation of the azo-compound, which was collected and purified after being washed with warm water:

0·1080 gave 10·2 c.c. N_2 at 17° and 750 mm. N = 11·1.

$C_{26}H_{25}N_3$ requires N = 11·1 per cent.

It is readily soluble in chloroform, benzene, or ether. In the presence of a small amount of ether the azo-compound dissolves in concentrated hydrochloric acid to yield an intense purplish-blue solution. After some time the colour disappears with the production of a dark precipitate which becomes red after keeping for a

further period. Concentrated sulphuric acid dissolves it with the production of an intense dark blue coloration, becoming red on dilution.

4-n-*Butylbenzeneazobenzoylacetone.*

A diazotised solution of 4-amino-*n*-butylbenzene (1 mol.), freed from nitrous acid by means of carbamide, was added to an alcoholic solution of benzoylacetone (1 mol.). The addition of sodium acetate produced a bright yellow turbidity, from which a dark-coloured oil separated. On keeping overnight in the ice-chest the oil solidified to a mass of dark yellow crystals which were collected, dried on a porous plate, and recrystallised. The compound separated from ether in stellate groups of yellow crystals melting at 97—100°:

0·1588 gave 12·2 c.c. N_2 at 18° and 747 mm. N = 8·9.

$C_{20}H_{22}O_2N_2$ requires N = 8·7 per cent.

The substance is soluble in alcohol or ether, and dissolves in sulphuric acid with the production of a brown colour, giving place to a yellow opalesceuce on dilution. Sulphuric acid containiug a small amount of dissolved chromic acid also produces a similar coloration.

4-n-*Butylbenzeneazo-2 : 7-dihydroxynaphthalene.*

This compound was obtained as a dark red powder on adding a solution of the diazotised amine to an alcoholic solution of 2:7-dihydroxynaphthalene in the presence of an excess of sodium acetate. It was purified by washing with a dilute aqueous solution of sodium hydroxide, followed by extraction with chloroform. It crystallised from hot glacial acetic acid in small, bronze-coloured crystals melting at 200—201°:

0·1588 gave 12·2 c.c. N_2 at 18° and 747 mm. N = 8·9.

$C_{20}H_{20}O_2N_2$ requires N = 8·7 per cent.

4-*Hydroxy*-n-*butylbenzene.*

4-Amino-*n*-butylbenzene (9 grams) was added to an aqueous solution containing sulphuric acid in excess (five molecular proportions), and, after cooling, diazotised by the addition of sodium nitrite. The mixture was stirred continuously, when the suspended sulphate gradually passed into solution. The solution was filtered to remove any unchanged sulphate, treated with a large excess of concentrated sulphuric acid, and subsequently distilled in a current of steam. 4-*Hydroxy*-n-*butylbenzene* passed over as a pale yellow oil, and was

obtained pure by distillation. It is an almost colourless oil, possessing a faint phenolic odour, and boiling at 248°/765 mm.:

0·0818 gave 0·2387 CO_2 and 0·0686 H_2O. C=79·6; H=9·3.
$C_{10}H_{14}O$ requires C=79·95; H=9·4 per cent.

4-n-*Butylphenyl Phenylcarbamate*, $C_4H_9 \cdot C_6H_4 \cdot O \cdot CO \cdot NHPh$.

4-Hydroxy-*n*-butylbenzene was heated on the water-bath with slightly more than one molecular proportion of phenylcarbimide. On cooling, the solid mass was passed on a porous tile and crystalised from alcohol, from which it separated in white needles melting at 115°:

0·1059 gave 4·7 c.c. N_2 at 20° and 744 mm. N=5·0.
$C_{17}H_{19}O_2N$ requires N=5·2 per cent.

2-*Nitro*-4-*amino*-n-*butylbenzene*.*

4-Amino-*n*-butylbenzene was dissolved in two hundred times its weight of concentrated sulphuric acid and, after cooling to −5°, the calculated amount of nitric acid (1 mol.), dissolved in three times its weight of sulphuric acid, was added gradually. During the addition of the acid the mixture was continually stirred, and the temperature not allowed to rise above 5°. After eighteen hours the mixture was poured into ice-water, when a sparingly soluble sulphate was precipitated, which was collected and decomposed by the addition of aqueous ammonia. In this way a brown, crystalline solid was obtained consisting of 2-*nitro*-4-*amino*-n-*butylbenzene*. A further quantity was isolated by treating the acid filtrate with aqueous ammonia and extracting the solution with ether. It was obtained pure by dissolving it in aqueous methyl alcohol, and precipitating with water, followed by recrystallisation from warm light petroleum (b. p. 80—100°). It forms golden-yellow scales, readily soluble in ether and melting at 52°:

0·0739 gave 9·3 c.c. N_2 at 17·5° and 735 mm. N=14·5.
$C_{10}H_{14}O_2N_2$ requires N=14·4 per cent.

No evidence was obtained of the existence of the other isomeride.

The *hydrochloride* was obtained as a white precipitate by adding hydrochloric acid to an ethereal solution of the base and evaporat-

* The nitration of *n*-butyl-*p*-toluidine has been previously described as yielding 2-*nitro*-*n*-*butyl*-*p*-*toluidine* as a red oil (T., 1918, **113**, 988). On keeping over the winter it solidified to a mass of bright red crystals melting at 18—19°. By converting the substance into its hydrochloride, crystallising from alcohol, and decomposing with aqueous ammonia, 2-nitro-*n*-butyl-*p*-toluidine was obtained in large, rectangular, red plates which melted at 19°.

ing the ether. It crystallises from warm absolute methyl alcohol in masses of slender, colourless needles. On heating, the colour changes to yellow. A specimen melted at 190—195° after immersion in the bath at 150°, a rapid darkening in colour taking place at 185—190°:

0·1017 gave 0·0638 AgCl. Cl = 15·5.

$C_{10}H_{14}O_2N_2,HCl$ requires Cl = 15·4 per cent.

The *sulphate* is sparingly soluble in dilute sulphuric acid. It crystallises from warm alcohol containing some sulphuric acid in small, white plates which are hydrolysed by water:

0·0811 gave 6·35 c.c. N_2 at 13·2° and 761 mm. N = 9·4.

$C_{12}H_{16}O_3N_2,H_2SO_4$ requires N = 9·6 per cent.

*2-Nitro-*n*-butylbenzene.*

2-Nitro-4-aminobutylbenzene (2·5 grams) was diazotised in aqueous alcoholic solution in the presence of sulphuric acid, a small amount of insoluble matter was removed, and the diazo-group was eliminated by heating with an excess of alcohol, when 2-*nitro*-n-*butylbenzene* was obtained. It is a pale yellow oil possessing a characteristically pleasant odour. It is readily volatile in steam, and apparently so in alcohol vapour, for on removing the alcohol by distillation after eliminating the diazo-group, appreciable amounts of the nitro-compound were obtained in the alcoholic distillate.

It distils with some decomposition at about 260° under the ordinary pressure:

0·0814 gave 5·4 c.c. N_2 at 20° and 746 mm. N = 7·6.

$C_{10}H_{13}O_2N$ requires N = 7·8 per cent.

*2-Amino-*n*-butylbenzene.*

Reduction of the nitro-compound was effected by means of zinc dust or tin foil and hydrochloric acid. The amine was isolated by extraction with ether after rendering the acid liquid alkaline. 2-*Amino*-n-*butylbenzene* is a yellow oil, possessing a rather unpleasant odour recalling that of aniline:

0·0746 gave 5·9 c.c. N_2 at 16° and 750 mm. N = 9·3.

$C_{10}H_{15}N$ requires N = 9·4 per cent.

The *acetyl* derivative crystallises from warm aqueous methyl alcohol in masses of small, white needles melting at 100°:

0·0819 gave 5·5 c.c. N_2 at 20·5° and 749 mm. N = 7·7.

$C_{12}H_{17}ON$ requires N = 7·3 per cent.

The melting point of this compound is very close to that of

4-acetylamino-*n*-butylbenzene. It was shown to be distinct from that substance, for a mixture of these acetyl derivatives commenced to melt at 75° and had completely melted at 85°.

3-*Nitro-4-amino-*n*-butylbenzene.*

The most convenient method of obtaining this compound in a pure state was to nitrate 4-acetylamino-*n*-butylbenzene by means of fuming nitric acid, afterwards eliminating the acetyl group.

3-*Nitro-4-acetylamino*-n-*butylbenzene.*—The acetyl compound (2 grams) was dissolved in 20 c.c. of glacial acetic acid, the solution cooled to −5°, and 15 grams of nitric acid (D 1·5) were added slowly, so that the temperature did not rise above 5°. After an hour the mixture was poured into ice-water, and the yellow precipitate collected. The nitro-compound is soluble in most of the common organic solvents except light petroleum, and crystallises very readily from hot alcohol in slender, canary-yellow needles melting at 76°:

0·0649 gave 6·8 c.c. N_2 at 20° and 746·6 mm. N = 12·0.

$C_{12}H_{16}O_3N_2$ reqnires N = 11·9 per cent.

Titration with Titanous Chloride.—0·01522 required 16·6 c.c. $TiCl_3$ (1 c.c. = 0·001297 gram Fe). Calc. as $C_{12}H_{16}O_3N_2$ = 100·4 per cent.

On triturating it in a mortar with a 50 per cent. solution of potassium hydroxide the colour changed from pale yellow to deep brown. After remaining for some time there was still a considerable amount of the unchanged acetyl derivative together with some 3-*nitro-4-amino-*n*-butylbenzene*. The latter compound was obtained more conveniently by hydrolysis with alcoholic hydrogen chloride. To the nitroacetyl compound dissolved in ten times its weight of alcohol, an amount of hydrochloric acid, insufficient to precipitate the nitro-compound, was added, and the mixture was heated under reflux until, on pouring into dilute hydrochloric acid, no precipitate was obtained. On evaporation, 3-nitro-4-amino-*n*-butylbenzene was left as a reddish-brown oil, which solidified in the ice-chest to a mass of reddish-yellow needles melting at about 13°. The substance was purified by converting it into the hydrochloride, and decomposing this with water or dilute ammonia:

0·0880 gave 11·0 c.c. N_2 at 18·5° and 745 mm. N = 14·4.

$C_{10}H_{14}O_2N_2$ requires N = 14·4 per cent.

Titration with Titanous Chloride.—0·01038 required 13·3 c.c. $TiCl_3$ (1 c.c. = 0·001344 gram Fe). Calc. as $C_{10}H_{14}O_2N_2$ = 100·8 per cent.

The *hydrochloride* crystallises from a mixture of alcohol and ether in flat, shining plates. It is readily hydrolysed by water.

Reduction of the base by adding zinc dust to a warm solution in hydrochloric acid gave 4-n-*butyl-o-phenylenediamine* as a viscous oil which is very readily oxidised on exposure to the air. On this account it was not isolated in a pure state for analysis, and the condensation product with benzil was prepared from its solution.

3-Nitro-4-amino-*n*-butylbenzene (1·4 grams) was dissolved in an excess of 50 per cent. aqueous acetic acid, and after raising the solution to the boiling point small quantities of zinc dust were added until the reduction was complete. Benzil (1·5 grams), dissolved in warm sodium hydrogen sulphite solution, was added and the mixture boiled for five minutes. A reddish-brown oil was produced, which on cooling settled to the bottom of the flask as a semi-solid mass. It was collected and, after pressing on a porous tile, crystallised from hot methyl alcohol. Pale yellow, flocculent masses of small crystals were obtained on rapid cooling and small, pale yellow needles, melting at 82°, by slow cooling. By spontaneous evaporation of an ethereal solution, large, well-defined groups of needle-shaped crystals separated:

0·0988 gave 6·8 c.c. N_2 at 15·0° and 768 mm. N = 8·3.
$C_{24}H_{22}N_2$ requires N = 8·3 per cent.

2:3-*Diphenyl*-6-n-*butylquinoxaline* (XVIII) is readily soluble in chloroform. It dissolves in cold, concentrated sulphuric acid with the production of an orange colour, which on dilution gives place to a white turbidity. It is also soluble in a large excess of concentrated hydrochloric acid, giving a yellow solution.

3-*Nitro*-n-*butylbenzene*.

3-Nitro-4-amino-*n*-butylbenzene was dissolved in hydrochloric acid (2·5 mols.) mixed with an equal volume of alcohol, and the solution cooled to −5°. A slight excess of sodium nitrite solution was added, and after about an hour some red, resinous matter was filtered off and the filtrate heated with an excess of ethyl alcohol under reflux for two hours. The alcohol was evaporated on the water-bath, and the volatile nitro-compound removed from the residue by distillation in a current of steam. 3-*Nitro*-n-*butylbenzene* was obtained as a yellow liquid having a pleasant odour:

0·0766 gave 5·4 c.c. N_2 at 20° and 747 mm. N = 8·1.
$C_{10}H_{13}O_2N$ requires N = 7·8 per cent.

The compound distils at 275°/752 mm. with no appreciable decomposition. It is apparently volatile to some extent in alcohol vapour, for on removing the excess of alcohol from the product of the diazo-reaction some of it was obtained in the distillate. It is

miscible with chloroform, nitrobenzene, pyridine, or light petroleum.

3-Amino-n-butylbenzene.

To the nitro-compound suspended in concentrated hydrochloric acid, small pieces of tin foil were added from time to time until the reduction was complete. The tin in solution was removed as sulphide, and after rendering the liquid alkaline with sodium hydroxide solution, the amine was removed by extraction with ether. It was further purified by distillation in a current of steam.

3-Amino-n-butylbenzene is a pale yellow oil, lighter than water, and possesses a faint, agreeable odour:

0·1454 gave 12·5 c.c. N_2 at 25° and 727 mm. N = 9·6.

$C_{10}H_{15}N$ requires N = 9·4 per cent.

The addition of an excess of warm concentrated hydrochloric acid yielded the *hydrochloride* as an oil which solidified on cooling to an interlaced mass of small, flattened, jagged needles.

The *acetyl* compound was obtained as an oil, which slowly hardened to a vitreous mass on keeping it in a desiccator:

0·0744 gave 4·9 c.c. N_2 at 25° and 745 mm. N = 7·4.

$C_{12}H_{17}ON$ requires N = 7·3 per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, separates from alcohol in small, white, needle-shaped crystals, which melt at 68°:

0·1610 gave 7·8 c.c. N_2 at 17° and 748 mm. N = 5·7.

$C_{17}H_{19}ON$ requires N = 5·5 per cent.

4-Amino-sec.-butylbenzene.

To show that no intramolecular rearrangement of the butyl group had occurred when *n*-butyl alcohol and aniline zincichloride interacted, the corresponding amine was prepared from *sec.*-butyl alcohol, which was obtained from *n*-butyl alcohol through the intermediate formation of butylene. In the presence of sulphuric acid, butylene yielded *sec.*-butyl alcohol, which was obtained pure by repeated fractionation. It boiled at 99·6—99·9°.

Aniline zincichloride was heated with one molecular proportion of *sec.*-butyl alcohol in an autoclave at 180° for sixty hours, the product being treated in exactly the same way as described above when *n*-butyl alcohol was used. The mixture of primary amines from the zincichloride was fractionated, and yielded, among other distillates, a fraction boiling between 230° and 250°. On redistilling this portion several times a primary amine was obtained boiling at 238°/762 mm. From the mixture of secondary amines soluble

in light petroleum, a primary amine was isolated by means of its sulphate, boiling at 238° and identical with the amine obtained from the mixture of primary bases:

0·1909 gave 16·0 c.c. N_2 at 19·5° and 740 mm. N=9·6.

$C_{10}H_{15}N$ requires N=9·4 per cent.

4-Amino-sec.-*butylbenzene*, on keeping, slowly changes in colour from very pale yellow to dark red. The diazonium salt gives a red *azo*-compound with β-naphthol in alkaline solution. With bleaching powder solution the amine gave no coloration. The addition of a solution of chromic acid in concentrated sulphuric acid produced a dirty green coloration, changing through purple to wine-red on dilution. Nitric acid added in small amount to the sulphate of the amine suspended in concentrated sulphuric acid coloured the solid matter purple, and the solution yellowish-brown.

The *hydrochloride* is precipitated from aqueous solution on the addition of an excess of hydrochloric acid:

0·0987 gave 0·0750 AgCl. Cl=18·8.

$C_{10}H_{15}N,HCl$ requires Cl=19·1 per cent.

The *sulphate* is sparingly soluble in cold water, but more readily so in hot water, from which it separates in masses of white crystals.

The *acetyl* derivative crystallises from aqueous alcohol in lustrous, white plates melting at 125—126°:

0·1540 gave 10·0 c.c. N_2 at 19° and 744 mm. N=7·5.

$C_{12}H_{17}ON$ requires N=7·3 per cent.

It is soluble in acetone, ether, or ethyl acetate, and sparingly so in water. No coloration is obtained by the addition of a solution of chromic acid in concentrated sulphuric acid.

With fuming nitric acid in glacial acetic acid solution it yields a yellow, crystalline *nitro*-derivative.

a-Phenyl-β-4-sec.-*butylphenylcarbamide*, $CHMeEt\cdot C_6H_4\cdot NH\cdot CO\cdot NHPh$.

This derivative is prepared by the addition of phenylcarbimide to 4-amino-*sec*.-butylbenzene. It crystallises from aqueous alcohol in silky needles melting at 144°:

0·0730 gave 6·5 c.c. N_2 at 14° and 756 mm. N=10·6.

$C_{17}H_{20}ON_2$ requires N=10·4 per cent.

It is soluble in ether, acetone, or toluene, but only sparingly so in light petroleum (b. p. 60—80°).

In addition to amino-*sec*.-butylbenzene, other amines were obtained from the product of the action of heat on the mixture of sec.-butyl alcohol and aniline zincichloride. At 270—280° a fraction

was obtained consisting mainly of a primary amine, which on further purification boiled mainly between 274° and 278°. This consisted apparently of aminodi-*sec.*-butylbenzene. A small quantity of a residue of a still higher boiling point was obtained, but it was not further investigated. The fractions of lower boiling points contained a considerable amount of a secondary amine, which was freed from the greater part of the primary amine by treatment with dilute sulphuric acid. In this manner a fraction was obtained boiling at 225—235° consisting chiefly of *sec.*-butylaniline, which was obtained in a pure state by the action of *sec.*-butyl chloride on aniline. Aniline (1 mol.) was heated under a reflux condenser with *sec.*-butyl chloride (1·5 mols.); this contained a small amount of dissolved iodine, and was added gradually over a period extending over twenty-four hours. The purplish-blue product was rendered alkaline, and from the ethereal extract the sec.-*butylaniline* was precipitated as the zincichloride, the base being purified by distillation. It distilled at 224—225°/765 mm. as an almost colourless oil which had a pleasant, floral odour distinct from that of the corresponding *n*-butyl derivative:

0·0928 gave 0·2732 CO_2 and 0·0866 H_2O. C=80·3; H=10·4.
0·0835 „ 6·7 c.c. N_2 at 14° and 756 mm. N=9·5.

$C_{10}H_{15}N$ requires C=80·5; H=10·1; N=9·4 per cent.

It is miscible with most of the common organic solvents. The addition of a solution of chromic acid in concentrated sulphuric acid led to the production of no characteristic coloration. On adding a small quantity of nitric acid to a solution of the amine in concentrated sulphuric acid a reddish-brown coloration was observed.

The *hydrochloride* was obtained as a hard, crystalline mass by saturating a benzene solution of *sec.*-butylaniline with dry hydrogen chloride:

0·1324 gave 0·1030 AgCl. Cl=19·2.

$C_{10}H_{15}N,HCl$ requires Cl=19·1 per cent.

It crystallises from warm benzene in hard nodules, which in bulk are grey. It is very readily soluble in water.

By the action of nitrous acid on the solution of the hydrochloride *phenyl*-sec.-*butylnitrosoamine* was obtained as a pale yellow oil, possessing an agreeable odour. It is volatile in steam:

0·0924 gave 12·6 c.c. N_2 at 18·7° and 753 mm. N=15·9.

$C_{10}H_{14}ON_2$ requires N=15·7 per cent.

p-sec.-*Butylphenol.*

On diazotising amino-*sec.*-butylaniline sulphate and boiling the solution, nitrogen was evolved, and the liquid assumed a reddish-

brown colour due to the production of *p-sec.*-butylphenol. It was purified by distillation in a current of steam, followed by fractionation.

At 238° *p-sec.*-butylphenol passed over as a pale oil, solidifying to a mass of long, hair-like, white needles, melting at 59°. The melting point was not altered after two crystallisations from light petroleum. (Estreicher, *Ber.*, 1900, **33**, 436, gives m. p. 53—54°, b. p. 239·5—240·5°/750·6 mm.) The substance is very readily soluble in alcohol or ether, and, when treated with a dilute solution of chromic acid in concentrated sulphuric acid, gives no characteristic coloration, other than the production of a transient red tint. Ferric chloride also gives no coloration. (Found: C=79·9; H=9·9. $C_{10}H_{14}O$ requires C=79·95; H=9·4 per cent.) It is miscible with most of the common organic solvents. This compound was also obtained, probably in an impure state, by the action of *n*-butyl alcohol on phenol. In this reaction a rearrangement of the alkyl group occurs.

The boiling point of the phenol agrees with that of the substance prepared by the diazo-reaction. It was not, however, obtained crystalline, nor were any crystalline derivatives prepared from it. It seems probable that *p-sec.*-butylphenol is not the only product of the interaction between *n*-butyl alcohol and phenol in the presence of zinc chloride.

Phenol (100 grams) was heated with fused zinc chloride (240 grams) and *n*-butyl alcohol (80 grams) for twelve hours. On cooling, the mixture had separated into two layers. The addition of water dissolved the lower layer consisting mainly of zinc chloride, whilst the dark-coloured oil was removed. It consisted chiefly of *p-sec.*-butylphenol, together with some ethers which were removed by dissolving the phenol in sodium hydroxide solution. On distillation the main fraction was collected between 235° and 245° as a colourless oil of agreeable odour. Further fractionation gave a colourless, viscous oil distilling at 237—240°.

On the addition of a diazotised solution of β-naphthylamine to a solution of the phenol in dilute potassium hydroxide solution, a brown liquid was obtained, from which a reddish-brown *azo*-compound was isolated on rendering acid and extracting with solvents. It was not, however, obtained in a pure state.

The acetyl derivative, prepared by heating 5 grams of *p-sec.*-butylphenol with an excess of fused sodium acetate and 10 grams of acetic anhydride for three hours, was obtained as a colourless oil boiling at 244—246°/760 mm. (Estreicher, *loc. cit.*, gives 255·5°/743·9 mm.).

The *benzoyl* derivative, obtained by the Schotten-Baumann method, is an almost colourless, viscous oil:

0·0686 gave 0·2023 CO_2 and 0·0430 H_2O. C=80·4; H=7·0.
$C_{17}H_{18}O_2$ requires C=80·3; H=7·1 per cent.

By nitrating crude *p-sec.*-butylphenol with concentrated nitric acid, mixtures of mono- and dinitro-derivatives were obtained. A better yield of the former was obtained by using dilute nitric acid.

p-sec.-Butylphenol (2·5 grams) was added to nitric acid (6 grams: D 1·5) and water (9 grams), the mixture being cooled in a stream of cold water. After sixteen hours the supernatant layer of acid was poured off and the residual oil distilled in a current of steam.

Nitro-p-sec.-*butylphenol* was obtained in this way as a red oil, which was purified by distillation under diminished pressure, when it distilled at 196—200°/80 mm.:

0·1452 gave 9·0 c.c. N_2 at 16° and 741 mm. N=7·2.
$C_{10}H_{13}O_3N$ requires N=7·2 per cent.

The addition of aqueous ammonia precipitated the *ammonium* salt, and solutions of sodium and potassium hydroxides precipitated the corresponding alkali salts.

Reaction with Phenylcarbimide.

By heating *p-sec.*-butylphenol, prepared from *n*-butyl alcohol, at 100° with one molecular proportion of phenylcarbimide, a viscous oil was obtained, which was purified by extracting it several times with light petroleum. It was dried first at 80° for a short time, and finally over solid potassium hydroxide under diminished pressure. On cooling to 0° it was obtained as a brittle solid which became viscous at the ordinary temperature.

Intramolecular Rearrangement of n-*Butylaniline.*

The experimental details for the production of 4-amino-*n*-butylbenzene have already been described (p. 110), and it has been mentioned that other substances are produced in the reaction. The primary amines which were separated by the use of zinc chloride were distilled. Aniline was obtained in the first fractions, the amount being dependent on the experimental conditions. The principal fraction was 4-amino-*n*-butylbenzene, but there was still a residue of amines boiling at above 270°; this, on distillation, proved to be a complex mixture, from which a primary amine boiling at 295—300° was isolated, and was probably 4-*amino*-1:3-*di*-n-*butylbenzene*:

0·0900 gave 5·3 c.c. N_2 at 20° and 737 mm. N = 6·7.
$C_{14}H_{23}N$ requires N = 6·8 per cent.

It yields a sparingly soluble *sulphate*, and after treatment with nitrous acid in the cold, combines with alkaline β-naphthol with the formation of an *azo*-compound. A fraction of still higher boiling point which also contains a primary amine was not investigated.

The ethereal washings of the zincichloride (p. 110) obtained by the action of *n*-butyl alcohol on aniline zincichloride were shaken with dilute sodium hydroxide solution to remove a portion (*A*) containing phenolic substances and then several times with dilute hydrochloric acid to remove a portion (*B*) containing secondary and tertiary amines. There was finally obtained an ethereal solution containing for the most part substances which are soluble only in concentrated hydrochloric acid, and are precipitated on dilution. These substances boil at above 290° under the ordinary pressure, and their sulphuric solution in the presence of nitrous acid develops an intense bluish-black colour. The behaviour and properties of these substances suggest that they may be diphenylamine derivatives, but they were not further investigated. The separated portions were examined as follows: (*A*) The phenolic substances were isolated by acidifying the alkaline solution and extracting with ether. They appeared to be a mixture of phenol and butylphenol, for on distillation two definite fractions were obtained, one at about 200—210°, and the principal fraction at 240—245°. These phenols do not appear to be constant constituents of the products of the reaction being usually present at the most in small amounts.

(*B*) The amines on distillation gave a secondary amine boiling at 235—245°, with small amounts of a primary amine at 255—265°, which was shown to be 4-amino-*n*-butylbenzene. Between 275° and 290° a secondary amine, probably 4-n-*butylamino*-n-*butylbenzene*, was collected in an impure condition. It was dissolved in dilute hydrochloric acid and treated with nitrous acid, when 4-n-*butylphenyl*-n-*butylnitrosoamine* separated as a yellowish-red oil, volatile in steam, and having a pleasant odour:

0·0703 gave 7·4 c.c. N_2 at 17·8° and 744 mm. N = 12·1.
$C_{14}H_{22}ON_2$ requires N = 12·0 per cent.

The amount of this secondary amine present in the mixture resulting from the action of *n*-butyl alcohol on aniline zincichloride is usually small, and the yield appears to depend on the experimental conditions. The residue of higher boiling point yielded, at about 300°, aminodibutylbenzene, which was isolated as a sparingly soluble sulphate, and a mixture of amines, yielding fractions up to 360°. Amines of still higher boiling points were obtained on dis-

tilling under diminished pressure until only a semi-carbonised mass remained in the flask. This distillate, which contained primary, secondary, and tertiary amines, was not further investigated, but no doubt consisted of amino-compounds containing more than two butyl groups in the nucleus.

The formation of 4-amino-*n*-butylbenzene by the action of dry *n*-butyl alcohol on aniline zincichloride may be due to the initial formation of *n*-butylaniline, followed by intramolecular change, or to the direct entry of the butyl group into the nucleus. The former suggestion agrees better with the experimental results, for by reducing the time of the reaction and the temperature at which it occurs *n*-butylaniline is obtained in greater amount than usual, whilst the yield of 4-amino-*n*-butylbenzene is much smaller. In one experiment the temperature was allowed to rise gradually to 180—200° over a period of six hours. The products were aniline and *n*-butylaniline, only a small quantity of 4-amino-*n*-butylbenzene being formed.

It was also fouud that pure *n*-butylaniline, in the presence of zinc chloride and also certain other salts, underwent intramolecular change on heating at temperatures between 200° and 240° for about six to eight hours.

n-*Butylaniline and Cobalt Chloride.*

n-Butylaniline (4·5 grams) was heated in a sealed tube at temperatures between 200° and 240° for seven hours with anhydrous cobalt chloride (2 grams). There was only a slight pressure on opening the tube, and the contents, which were initially pale green, changed to a deep blue, crystalline mass. After treatment with warm water and dilute sodium hydroxide solution the mixture of amines had the following composition:

Primary amine	62 per cent.
Secondary amine	14 „ „
Bases insoluble in dilute hydrochloric acid ...	23 „ „

The primary amine gave an acetyl compound melting at 103° after one crystallisation, which was identical with 4-acetylamino-*n*-butylbenzene.

Other experiments were carried out, by heating pure *n*-butylaniline under pressure in the presence of various substances, such as zinc chloride and sodium chloride. The results obtained are given in the following table:

Substance added.	Duration of heating.	Percentage composition of resulting amines. Primary.	Secondary.	Insoluble in dilute acid.
—	8 hours.	1	99	—
NaCl	8 ,,	—	100	—
SiO_2	8 ,,	1	99	—
$CaSO_4$	8 ,,	—	100	—
$CaCl_2$	8 ,,	2	98	—
$CoCl_2$	7 ,,	62	14	23
$CuCl_2$	8 ,,	11	*	50
$ZnCl_2$	7 ,,	47	37	16
$CoCl_2$	8 ,,	50	20	30
$HgCl_2$	8 ,,	20	*	*

* Not determined.

The temperature in every case varied between 200° and 240° except in the case of *n*-butylaniline, which was heated alone at 240—260°. The experiments are, however, not comparable. When the amine was heated with cupric chloride the mixture at the end of the reaction was very dark and contained small, bright red, metallic particles, presumably of copper. The yield of amines insoluble in dilute hydrochloric acid was also high. In the experiment with mercuric chloride some metallic mercury was obtained.

It was observed that the intramolecular rearrangement of the butylaniline was accompanied by the combination of the secondary amine with the substance added. Some of these additive compounds have been isolated.

n-*Butylaniline cobaltochloride* was obtained by heating butyliniline with an excess of finely powdered anhydrous cobalt chloride n the presence of chloroform. After collecting the excess of suspended metallic salt, the chloroform solution was evaporated to dryness, when the cobaltochloride was obtained as a greenish-blue, itrecus mass, which becomes viscous after heating at 100°. It is ecomposed by water with the formation of cobalt chloride and utylaniline:

0·4226 gave 0·4265 AgCl. Cl = 25·0.

$C_{10}H_{15}N,CoCl_2$ requires Cl = 25·4 per cent.

n-*Butylaniline zincichloride* was obtained as a grey, vitreous mass y heating *n*-butylaniline in chloroform solution with an excess of nc chloride. The solution was filtered from the zinc chloride and e solvent removed by distillation. On washing with small quanties of light petroleum to remove the excess of butylaniline, the ncichloride remained in a pure condition:

0·1450 gave 0·1458 AgCl. Cl = 24·9.

$C_{10}H_{15}N,ZnCl_2$ requires Cl = 24·9 per cent.

n-Butylaniline and cadmium chloride also form an additive com-

pound, which in common with those of the chlorides of cobalt and zinc is readily decomposed by hot water. The instability of the zincichloride toward water explains the readiness with which primary amines may be separated from secondary by the use of zinc chloride.

Evidence was obtained of the formation of compounds with ferric chloride and cupric chloride by warming the chlorides with a chloroform solution of butylaniline. With ferric chloride a very dark green substance was obtained, soluble in aqueous alcohol (75 per cent.), giving a bright green colour. Cupric chloride gave a deep violet chloroform solution, yielding a solid which was almost black.

With the chlorides of calcium or sodium, or with calcium sulphate and silica, no indications were obtained of the formation of additive compounds.

Additive Compounds of 4-Amino-n-butylbenzene with Metallic Salts.

The products of intramolecular change apparently contained additive compounds of the primary amine with the salt employed. A few of these compounds were prepared and analysed.

4-Amino-n-butylbenzene zincichloride was obtained as a caseous mass by adding an aqueous solution of zinc chloride to 4-amino-*n*-butylbenzene:

0·2355 gave 0·1540 AgCl. Cl = 16·2.

$(C_{10}H_{15}N)_2ZnCl_2$ requires Cl = 16·3 per cent.

It is sparingly soluble in water, alcohol, or ether. Dilute acids hydrolyse it rapidly.

4-Amino-n-butylbenzene cobaltochloride was prepared by mixing alcoholic solutions of anhydrous cobalt chloride with an excess of the base. After being crystallised from absolute methyl alcohol, it formed a bright blue powder which is decomposed by water into its components, slowly in the cold, but more quickly on warming:

0·0858 gave 0·0562 AgCl. Cl = 16·2.
0·2155 ,, 0·0793 $CoSO_4$. Co = 14·0.

$(C_{10}H_{15}N)_2,CoCl_2$ requires Cl = 16·6; Co = 13·8 per cent.

4-Amino-n-butylbenzene cadmichloride was obtained as a white, bulky mass by mixing the components in methyl-alcoholic solution. It crystallises from hot methyl alcohol in small, white crystals with a nacreous lustre, and tends to form crusts of crystals on the surface of the solution. It is hydrolysed on boiling with water.

Action of Heat on n-Butylaniline Hydrochloride.

Crude mono-*n*-butylaniline was converted into its hydrochloride by evaporating it with an excess of concentrated hydrochloric acid until the solution was of a syrupy consistency. On keeping overnight it had solidified to a hard mass of crystals, which were transferred to a retort and heated in an oil-bath at 260—300°. The disengaged vapours were passed through a condenser to remove any liquid. A considerable amount of a liquid was condensed, nearly all of which boiled between 80° and 83°, indicating the presence of *n*-butyl chloride. The gas which escaped condensation was passed through bromine, and after removing the excess of bromine by means of sodium hydrogen sulphite, a small amount of a colourless liquid was obtained, which was not further examined. In this experiment an excess of hydrochloric acid was originally present. Another experiment was carried out taking precautions to avoid an excess. The hydrochloride was dried on a steam-bath for twelve hours, and exposed to the air for a further period, after which it was heated at 280—300° for one hundred hours. During the earlier stages of the experiment, a liquid (*A*) was condensed, which became darker as the heating proceeded. The gas evolved was passed through bromine, when a liquid dibromide was obtained in small amount.

From the distillate (*A*) there separated a small quantity of flat, grey crystals, which consisted of aniline hydrochloride. The liquid portion, after being rendered alkaline, gave, on distillation, a fraction boiling between 70° and 80°, chiefly at 77—80°, which was *n*-butyl chloride. There was also a fraction boiling chiefly between 200° and 250°, containing principally a primary amine mixed with some secondary, the former being identified as aniline.

The residue in the flask, which was black and tarry, was rendered alkaline, and the resulting amine treated with an excess of zinc chloride solution, in order to separate the primary amines from the other products. The insoluble zincichlorides gave a mixture of amines boiling between 200° and 255°, and yielding a considerable fraction at 240—255°. The ethereal washings of the zincichloride contained a secondary amine, boiling between 230° and 250°, whilst at 250—260° a mixture of primary and secondary amines was obtained. There were also present bases which were insoluble in dilute hydrochloric acid, but soluble in the concentrated acid, and were probably diphenylamine derivatives.

Preparation of n-Butylaniline Hydrochloride.

n-Butylaniline hydrochloride has previously been obtained by Kahn (*Ber.*, 1885, **18**, 3361) by evaporating a solution of *n*-butyl-

aniline in hydrochloric acid to crystallisation. A more convenient method was to pass a stream of dry hydrogen chloride into a solution of butylaniline in an equal volume of benzene or toluene. A considerable amount of heat was generated, sufficient to evaporate some of the hydrocarbon. On cooling, *n*-butylaniline hydrochloride crystallised out, and was collected, washed, and dried. The filtrate, which still contained much of the salt, was precipitated by the addition of ether, when the hydrochloride was obtained in very small, white crystals having a silvery appearance. They were collected, washed with further amounts of ether, and dried, first at 60° and later at 100°.

n-Butylaniline hydrochloride crystallises in very small, irregular plates from hot ethyl acetate, in which it is readily soluble. It is only moderately soluble in the cold solvent.

Comparative Experiments on Alkylarylamines with various Alkyl Groups.

A comparison was made of the stability of alkylarylamines containing alkyl groups of different weight. For this purpose methyl- and *n*-butyl-arylamines were employed. In the earlier investigations the experiments were carried out on the intramolecular rearrangement of methyl- and *n*-butyl-aniline. The secondary amines were heated in sealed tubes with a molecular proportion of substances which aid the formation of aminoalkylbenzenes. The tubes were arranged in iron shields in such a manner that the temperature and the duration of heating were approximately the same in each case. The results are given in the following table. The results show that there is a difference, although not very marked, in the behaviour of the two amines, *n*-butylaniline undergoing intramolecular change more readily. In this case the action is characterised by the formation of appreciable quantities of substances of the nature of diphenylamine, which are either absent in the case of methylaniline or present only in small amount.

		n-Butylaniline.		Methylaniline.	
Substance added.	Time of heating.	Primary. Per cent.	Secondary. Per cent.	Primary. Per cent.	Secondary. Per cent.
$CoCl_2$	5 hours.	73	10	57	32
$CdCl_2$	6 ,,	52	24	43	24
HCl	6 ,,	*	20	—	95
HCl	8 ,,	68	18	23	*
$CoCl_2$ (½ mol.)	5 ,,	*	33	*	50
HCl	4 ,,	*	33	*	49

* Not estimated.

It was observed that methylaniline yields additive compounds with cobalt chloride, zinc chloride, and cadmium chloride similar to those described in the case of *n*-butylaniline (p. 126).

Methylaniline cobaltochloride was obtained as a dull blue powder on triturating anhydrous cobalt chloride with an excess of freshly distilled methylaniline and heating the mixture on a steam-bath for a short time, the excess of methylaniline being then extracted by means of chloroform. On long keeping, the salt became greenish-yellow:

0·1157 gave 0·1402 AgCl. Cl = 30·0.
0·4312 „ 0·2818 $CoSO_4$. Co = 24·9.

$C_7H_7N,CoCl_2$ requires Cl = 30·2; Co = 25·1 per cent.

Methylaniline cadmichloride was prepared in a similar way. It is a white powder, which is decomposed by water:

0·4099 gave 0·4016 AgCl. Cl = 24·2.
0·3045 „ 0·2150 $CdSO_4$. Cd = 39·0.

$C_7H_7N,CdCl_2$ requires Cl = 24·6; Cd = 39·0 per cent.

In the formation of the additive compounds of alkylanilines with metallic salts, the steric effects of the alkyl group may affect the formation of the compounds to a different extent, and for this and other reasons (difficulty of ensuring the same temperature and pressure in each tube) the experiments are probably not strictly comparable. The comparison of the relative stability of methyl and *n*-butyl groups was therefore carried out with tertiary amines, such as methyl-*n*-butylaniline. The intramolecular rearrangement of this compound proceeds in two stages, namely, the formation of a secondary amine, followed by conversion into a primary amine. It therefore became necessary to prepare the compounds that may possibly occur in the mixture.

Methyl-n-*butylaniline.*

This substance was prepared in three ways, namely, by the interaction of (*a*) *n*-butyl bromide and methylaniline, (*b*) *n*-butyl chloride and methylaniline, (*c*) methyl iodide and *n*-butylaniline, and the products in each case were the same. It was found that to obtain pure methyl-*n*-butylaniline by distillation was a tedious operation leading to losses. In the earlier work the process of purification consisted in converting the crude methyl-*n*-butylaniline into its picrate, and then crystallising the picrate until pure. This procedure was abandoned later and the secondary amine was removed by heating the crude tertiary amine with a slight excess of the theoretical amount of phenylcarbimide. The excess of the reagent was removed by warming with water, followed by distillation in a cur-

rent of steam. *Methyl*-n-*butylaniline* was obtained in this way as a pale yellow, refractive liquid boiling at 242—243°/766 mm.:

0·1071 gave 0·3180 CO_2 and 0·0987 H_2O. C=81·0; H=10·3.
0·0988 „ 7·7 c.c. N_2 at 28° and 748 mm. N=8·8.
$C_{11}H_{17}N$ requires C=80·9; H=10·5; N=8·6 per cent.

The *hydrochloride* was obtained as an oil on passing a stream of dry hydrogen chloride into an ethereal solution of the base. After repeated washings with small quantities of dry ether, and keeping over potassium hydroxide under diminished pressure, it solidified to a mass of white, glistening laminæ:

0·1633 gave 0·1170 AgCl. Cl=17·7.
$C_{11}H_{17}N,HCl$ requires Cl=17·8 per cent.

It is extremely soluble in water or alcohol, moderately so in nitrobenzene, and sparingly so in toluene.

From an aqueous solution of the hydrochloride containing a slight excess of free acid, the *platinichloride* was obtained as an orange-yellow precipitate sparingly soluble in water:

0·1152 gave 0·0304 Pt. Pt=26·4.
0·2234 „ 7·0 c.c. N_2 at 18° and 738 mm. N=3·6.
$(C_{11}H_{17}N)_2,H_2PtCl_6$ requires Pt=26·5; N=3·8 per cent.

The *picrate* crystallises from a methyl-alcoholic solution of the components in small, yellow crystals melting at 90°.

Titration with Titanous Chloride.—0·010 required 20·3 c.c. $TiCl_3$ (1 c.c. $TiCl_3$=0·001257 gram Fe). Calc. as $C_{11}H_{17}N,C_6H_3O_7N_3$= 100·5 per cent.

The melting point of this compound differs from that recorded by Komatsu (*loc. cit.*), who gives 141—142°. The picrates from the amine obtained by introducing the alkyl groups in different order were found to be identical, and a mixture of them also melted at 90°.

p-*Nitrosomethyl*-n-*butylaniline.*—Nitrous acid acted on a solution of methyl-*n*-butylaniline hydrochloride containing free hydrochloric acid yielding a reddish-brown solution, and the addition of ice-cold dilute aqueous ammonia precipitated the base as an oil, which was removed by means of ether. It was obtained as a greenish-blue liquid, which was steel-blue by reflected light:

0·1184 gave 0·2981 CO_2 and 0·0909 H_2O. C=68·7; H=8·5.
0·1282 „ 16·2 c.c. N_2 at 15° and 745 mm. N=14·8.
$C_{11}H_{16}ON_2$ requires C=68·7; H=8·4; N=14·6 per cent.

On heating the base under reflux with an excess of a 10 per cent. aqueous solution of sodium hydroxide, decomposition occurred with the production of a volatile amine, probably methyl-*n*-butylamine.

4-*Methylamino*-n-*butylbenzene* was obtained by heating 4-amino-

n-butylbenzene with methyl iodide. The addition of a dilute solution of sodium hydroxide liberated the base as an almost colourless oil boiling at 262—265°/760 mm.:

0·1042 gave 7·6 c.c. N_2 at 15° and 759 mm. N=8·7.
$C_{11}H_{17}N$ requires N=8·6 per cent.

By the action of nitrous acid 4-n-*butylphenylmethylnitrosoamine* $C_{11}H_{16}ON_2$, was obtained as a pale yellow oil. This was nitrated by dissolving it in glacial acetic acid, and cautiously adding ten times its weight of fuming nitric acid in the cold. After a short time the reaction was completed by heating on the water-bath until the mixture was pale red or yellow. This was then poured on crushed ice and the nitro-derivative collected and crystallised by dissolving it in cold fuming nitric acid. On keeping, *dinitro*-n-*butylphenyl*-4-*methylnitroamine*, $C_{11}H_{14}O_6N_4$, was obtained in pale yellow plates. From warm glacial acetic acid it crystallises in very pale yellow, glistening plates at 86°.

Ethyl-n-*butylaniline* was obtained by the action of *n*-butyl chloride on ethylaniline and also by allowing ethyl iodide to react with butylaniline. It was obtained pure in the manner described for methylbutylaniline, and is a pale yellow oil boiling at 248°/768 mm.:

0·0968 gave 0·2880 CO_2 and 0·0891 H_2O. C=81·1; H=10·2.
0·0836 ,, 5·9 c.c. N_2 at 25° and 748 mm. N=8·0.
$C_{12}H_{19}N$ requires C=81·3; H=10·8; N=7·9 per cent.

The *picrate* crystallises from aqueous alcohol in bright yellow, thin prisms or narrow plates melting at 100°:

0·010 required 20·0 c.c. $TiCl_3$ (1 c.c. $TiCl_3$=0·00125 gram Fe). Calc. for $C_{12}H_{19}N,C_6H_3O_7N_3$=99·3 per cent.

p-*Nitrosoethyl*-n-*butylaniline* was obtained as an oil having a dark blue, metallic colour when viewed by reflected light:

0·017 gave 12·1 c.c. N_2 at 24° and 741 mm. N=13·7.
$C_{12}H_{18}ON_2$ requires N=13·6 per cent.

p-*Nitrosoethyl*-n-*butylaniline zincichloride* was prepared by mixing alcoholic solutions of the components and evaporating the alcohol under diminished pressure, but it was not obtained crystalline.

4-*Ethylamino*-n-*butylbenzene* is a liquid of agreeable odour and boiling at 270—272°/762 mm.:

0·1024 gave 7·5 c.c. N_2 at 22° and 746 mm. N=8·2.
$C_{12}H_{19}N$ requires N=7·9 per cent.

The *nitrosoamine* is a yellow oil:

0·0999 gave 11·65 c.c. N_2 at 20° and 746 mm. N=13·4.
$C_{12}H_{18}ON_2$ requires N=13·6 per cent.

2-Amino-5-n-butyltoluene.

Molecular proportions of *n*-butyl alcohol and *o*-toluidine were heated at 200—240° for twenty-four hours, and the mixture was treated in the manner already described for 4-amino-*n*-butylbenzene. *2-Amino-5-n-butyltoluene* was obtained as a very pale yellow liquid boiling at 265—268°/765 mm.:

0·0960 gave 7·1 c.c. N_2 at 20° and 757 mm. N = 8·6.
$C_{11}H_{17}N$ requires N = 8·6 per cent.

The *hydrochloride* crystallises from warm dilute hydrochloric acid in rosettes of white needles:

0·1176 gave 0·0840 AgCl. Cl = 17·8.
$C_{11}H_{17}N,HCl$ requires Cl = 17·8 per cent.

It is precipitated from aqueous solution by the addition of an excess of hydrochloric acid.

The *acetyl* derivative crystallises from dilute aqueous alcohol in white masses of crystals melting at 89°:

0·1039 gave 6·0 c.c. N_2 at 15° and 750 mm. N = 6·8.
$C_{13}H_{19}ON$ requires N = 6·8 per cent.

On diazotising the hydrochloride and adding the solution to alkaline β-naphthol, *5-n-butyltoluene-2-azo-β-naphthol* is precipitated. It crystallises from hot glacial acetic acid in bulky masses of small, bright red needles melting at 105—107°. It is only moderately soluble in alcohol, and dissolves in concentrated sulphuric acid with the production of a purple coloration.

4-Amino-3-n-butyltoluene.

This amine was obtained by the action of *n*-butyl alcohol on *p*-toluidine zincichloride, in the manner already described for the preparation of 4-amino-*n*-butylbenzene. It is a liquid boiling at 265—270° under atmospheric pressure:

0·1496 gave 11·3 c.c. N_2 at 19° and 762 mm. N = 8·9.
$C_{11}H_{17}N$ requires N = 8·6 per cent.

The *acetyl* derivative separates as a white mass on cooling the product of interaction of 4-amino-3-*n*-butyltoluene and acetic anhydride. It crystallises from alcohol in tufts of white, slender needles melting at 129°:

0·1113 gave 0·3105 CO_2 and 0·0953 H_2O. C = 76·1; H = 9·5.
$C_{13}H_{19}ON$ requires C = 76·0; H = 9·3 per cent.

*The Intramolecular Rearrangement of Methyl-*n*-butylaniline.*

Pure methyl-*n*-butylaniline was heated in a sealed tube with on molecular proportion of either zinc chloride or cobalt chloride. Ii one experiment methyl-*n*-butylaniline hydrochloride was employed The temperature varied between 200° and 250°, and the heating wa: allowed to continue for about six to eight hours. On opening th(tubes there was usually a pressure due to the presence of an inflammable gas. The contents of the tube were rendered alkaline, and the amines were obtained by distillation in a current of steam. The mixture of amines obtained in this way was treated with zinc chloride solution, which removed the bulk of the primary amines. The ethereal washings of the zincichloride were washed with dilute hydrochloric acid to remove primary, secondary, and tertiary amines. From this acid solution the secondary amines were separated as nitrosoamines and the primary amines converted into the corresponding diazonium salts.

The nitrosoamines separated in this way were nitrated, yielding in each case an oily product, which was obtained crystalline only on keeping in contact with concentrated nitric acid for several days. By pressing on a porous tile to remove oily impurities, and by repeated recrystallisation from glacial acetic acid, a small amount of a pale yellow, crystalline substance was obtained melting at 93°, and the melting point was raised to 94—95° by the addition of 3:5-dinitro-*p*-tolyl-*n*-butylnitroamine. It is probable that the latter compound was present in the nitration product, indicating the existence of *n*-butyl-*p*-toluidine in the mixture of amines from the intramolecular rearrangement of methyl-*n*-butylaniline. It was not found possible to isolate any other nitro-compound in a pure state from the mixture, although appreciable amounts were present.

It is probable that in the mixture dinitro-*n*-butylphenylmethylnitroamine was also present, as only *n*-butyl-*p*-toluidine and 4-methylamino-*n*-butylbenzene would be expected to occur in any appreciable amount.

In one case small amounts of 2:4:6-trinitrophenylmethylnitroamine were isolated, and the primary amine from it indicated *p*-toluidine. By crystallisation of the azo-compounds from this experiment, *p*-tolueneazo-β-naphthol, melting at 129°, was isolated, and this melting point was not depressed by the addition of pure *p*-tolueneazo-β-naphthol. The small amounts of derivatives of methylaniline and *p*-toluidine isolated were due probably to the rearrangement not proceeding to completion.

Action of Heat on Methyl-n-butylaniline Hydrochloride.

Methyl-*n*-butylaniline (4·2 grams) was dissolved in an excess of concentrated hydrochloric acid in a small glass retort, which was heated in an oil-bath at 150—200°, a stream of hydrogen chloride being allowed to pass through the retort during the period of heating. A portion of the residue in the vessel was removed, and after diluting and adding more hydrochloric acid it was cooled to 0° and treated with a slight excess of an aqueous solution of sodium nitrite. A nitrosoamine separated, which was removed by extraction with ether. The ethereal solution was washed several times with water and dilute sodium hydroxide, dried, and evaporated, and the residue was dissolved in glacial acetic acid, nitrated by heating it on a water-bath with fuming nitric acid, until the colour of the mixture had changed to a pale red. On pouring the mixture into water an oily product was obtained which, when crystallised from fuming nitric acid, melted at 90—92°. The addition of trinitrophenylbutylnitroamine (m. p. 99°) depressed the melting point to about 89—92°, whilst the addition of trinitrophenylmethylnitroamine raised the melting point to 110—115°. The secondary amine resulting from the elimination of alkyl groups from methylbutylaniline in a stream of hydrogen chloride is therefore probably a mixture of methyl- and butyl-aniline.

The further examination of the products of this reaction is deferred until the physical constants of mixtures of trinitrophenylmethylnitroamine and trinitrophenylbutylnitroamine have been determined.

The Nitration of Dialkylanilines.

The method usually adopted to nitrate dissimilarly substituted dialkylanilines was to add cautiously about 10 to 15 times their weight of fuming nitric acid to a solution in glacial acetic acid. The reaction was completed by heating on the water-bath until the dark colour of the mixture had given place to a pale yellow or red. The nitration product was then isolated by pouring on ice, when it was collected and purified by crystallisation from fuming nitric acid.

Dibutylaniline, when treated in this way, gave *trinitrophenyl-n-butylnitroamine* in very pale yellow plates melting at 100°:

0·1093 gave 20·3 c.c. N_2 at 20° and 748 mm. N = 21·3.

$C_{10}H_{11}O_8N_5$ requires N = 21·3 per cent.

It is soluble in alcohol or acetone, and can be conveniently recrystallised from hot glacial acetic acid. An alcoholic solution of

sodium hydroxide in the cold gives a deep orange-red coloration. It dissolves in cold concentrated sulphuric acid without any development of colour, but on dilution a yellow turbidity is produced.

This substance was shown to be identical with the nitro-derivative obtained on nitrating phenyl-*n*-butylnitrosoamine. It was also obtained by nitrating dibutylaniline in the presence of nitric and sulphuric acids. Dibntylaniline (10 grams) dissolved in concentrated sulphuric acid (18 grams) was slowly added to a mixture of sulphuric (50 grams) and nitric acids (150 grams), the temperature being maintained between 35° and 45° throughout the reaction. After all the amine had been added the mixture was maintained for some time at 50°, and then thrown on crushed ice, when the nitro-compound was collected as a viscous, red substance and purified in the usual manner by crystallisation from fuming nitric acid. The strongly acid aqueous portion was found to contain butyric acid. The nitro-compound was removed by filtration through a thick layer of glass-wool. It was found necessary to take these precautions to remove the last traces of the nitro-compound in order to prevent contamination of the products at a later stage. To the acid filtrate, iron filings were added gradually, care being taken to avoid a too-vigorous action. After remaining overnight, the solution was distilled in a current of steam. The distillate, which still contained a small amount of nitric acid, was neutralised and evaporated to a small bulk. It was then rendered acid by adding an excess of sulphuric acid, and the last traces of nitric acid were removed by a further treatment with iron filings. A further distillation in a current of steam gave a distillate which contained a volatile acid, and this was identified by means of its "distillation constant" determined in an apparatus described by the authors (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 513). The constant agreed with that for *n*-butyric acid mixed with a small proportion of an impurity, and its presence was confirmed by its odour and by its reaction with ferric chloride.

Comparative experiments were also carried out, using dimethylaniline. Methyl-*n*-butylaniline was nitrated by fuming nitric acid dissolved in glacial acetic acid following the method described above. The product melted at 123—125° after crystallisation from fuming nitric acid. It was recrystallised from glacial acetic acid, and was found to be identical with 2:4:6-trinitrophenylmethylnitroamine, for no depression of the melting point occurred when a mixture was prepared with this nitro-compound and trinitrophenylmethylnitroamine from another source.

Ethyl-n-butylaniline, on nitration with fuming nitric acid or with

a mixture of nitric and sulphuric acids, gave a product which, on crystallisation from fuming nitric acid, furnished a mixture yielding trinitrophenyl-*n*-butylnitroamine on crystallisation from glacial *acetic* acid.

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XVI.—*The Condensation of Ethyl Acetoacetate with* p-*Dimethylaminobenzaldehyde and Ammonia.*

By LEONARD ERIC HINKEL and HERBERT WILLIAM CREMER.

THIS work was interrupted by the war, and as there seems no possibility of it being continued jointly, it was considered advisable to place on record such results as were obtained. The investigation arose from a desire to study the influence of substituent groups in aliphatic and aromatic aldehydes in Hantzsch's pyridine condensation. It was thought that the introduction of basic groups would retard it, and for this purpose *p*-dimethylaminobenzaldehyde was chosen.

The condensation was found to take place very slowly even on heating, the best results being obtained by allowing the mixture to remain for about one hour at the ordinary temperature and then heating under pressure for seven to nine hours. The yield of the dihydro-derivative could not be increased by longer heating or by employing excess of ammonia. The viscous filtrate from the dihydro-compound was subjected to steam distillation, but no aldehyde passed over with the steam. The filtrate was soluble in hydrochloric acid and reprecipitated unchanged by alkali. In all probability, the filtrate contained a *cyclo*-ketone formed by the further condensation of the 1:5-diketone first produced along with the dihydro-compound. The filtrate was not further examined. The dihydro-derivative can also be produced by condensing the aldehyde with ethyl acetoacetate (1 mol.) and ethyl β-aminocrotonate (1 mol.). This method was also employed with *p*-dimethylaminobenzaldehyde, and also, for comparison, with benzaldehyde. In the first case, the yield was 21·7 per cent., whilst with benzaldehyde it was more than 90 per cent., showing in a striking manner the effect of the *p*-dimethylamino-group on the condensation. The oxidation of the dihydro-derivative could not be carried out according to the usual method by nitrous fumes. Even at low temperatures, brown, needle-shaped crystals readily

formed, which were found to be *p*-nitrosodimethylaniline nitrate. The readiness with which the *p*-dimethylaminophenyl group is eliminated is probably due to the influence exerted by the dimethylamino-group, since it has been shown (Schiff and Puliti, *Ber.*, 1883, **16**, 160; Epstein, *Annalen*, 1885, **231**, 1) that phenyl- and styryldimethyldihydropyridinedicarboxylic esters are readily oxidised by nitrous fumes without elimination of the phenyl or styryl groups.

EXPERIMENTAL.

Ethyl 4-p-*Dimethylaminophenyl*-2:6-*dimethyl*-1:4-*dihydropyridine*-3:5-*dicarboxylate*,

$$\begin{array}{c} CO_2Et\cdot \overset{}{C}\cdot CH(C_6H_4\cdot NMe_2)\cdot C\cdot CO_2Et \\ \| \qquad\qquad\qquad\qquad \| \\ CMe\text{———}NH\text{———}CMe \end{array}$$

A mixture of 30 grams (1 mol.) of *p*-dimethylaminobenzaldehyde, 52 grams (2 mols.) of ethyl acetoacetate, 3·4 grams (1 mol.) of ammonia, and 70 c.c. of alcohol, contained in a closed flask, was allowed to remain for an hour and then heated for nine hours over a rapidly boiling water-bath. Considerable pressure was developed in the flask, which was therefore suitably protected against explosion. On cooling, about half of the contents of the flask crystallised, and the crystals were collected and washed with a small quantity of alcohol. The residue was evaporated over a water-bath until viscid, and, when cold, diluted with an equal volume of alcohol; on stirring, a small, further quantity was obtained, the total yield being 40 grams, or 53·7 per cent. of the theoretical. The crude, yellow crystals were purified by crystallisations from alcohol, acetone, and ethyl acetate, and were obtained finally in nearly colourless, fine needles melting at 158·5°:

0·2452 gave 0·6047 CO_2 and 0·1702 H_2O. C=67·26; H=7·7.
0·1617 „ 10·8 c.c. N_2 (moist) at 7·5° and 750 mm. N_2=8·0.
$C_{21}H_{28}O_4N_2$ requires C=67·64; H=7·52; N=7·52 per cent.

The ester is very similar to the trimethyl ester prepared by Hantzsch. It is stable to boiling dilute alkali, and boiling alcoholic potassium hydroxide slowly acts on it, bringing about complete decomposition. When heated with concentrated hydrochloric, sulphuric, or phosphoric acid, the compound is also decomposed, with the elimination of two molecular proportions of carbon dioxide. By virtue of the dimethylamino-group, however, it possesses basic properties and readily forms sparingly soluble additive compounds with hydrogen chloride and with methyl iodide.

Condensation of p-*Dimethylaminobenzaldehyde, Ethyl Acetoacetate, and Ethyl β-Aminocrotonate.*

A mixture of 6 grams (1 mol.) of *p*-dimethylaminobenzaldehyde, 5·2 grams (1 mol.) of ethyl acetoacetate, and 4·5 grams (1 mol.) of ethyl β-aminocrotonate was heated at 120° for several hours. After two days, the viscous mass was dissolved in an equal volume of hot alcohol and left to crystallise. The product, after recrystallisation from ethyl acetate, was identical with the ester just described, the yield being 3·2 grams, or 21·7 per cent. of the theoretical.

The *hydrochloride*, $C_{21}H_{28}O_4N_2,HCl$, prepared by dissolving the substance in dilute hydrochloric acid, separates as a fine, white, crystalline powder, especially on dilution with water. It was washed with water and alcohol, and dried in a vacuum:

0·1827 gave 0·4130 CO_2 and 0·1257 H_2O. C=61·6; H=7·63.
0·1613 „ 9·4 c.c. N_2 (moist) at 14° and 751 mm. N=6·85.
0·1466 „ 0·0527 AgCl. Cl=8·60.
$C_{21}H_{28}O_4N_2,HCl$ requires C=61·68; H=7·09; N=6·85; Cl=8·68 per cent.

It melts at 201°, and, when heated above its melting point, rapidly decomposes, yielding dimethylaniline among the products.

Methiodide, $C_{21}H_{28}O_4N_2,CH_3I$.—A mixture of the substance with excess of methyl iodide in acetone solution was gently heated for a short time over a water-bath. The clear, hot liquid was then poured into an evaporating basin and stirred with a glass rod until the mass solidified. The crude methiodide was washed with acetone and purified by crystallisation from hot acetone, and finally from ethyl acetate. It melts at 182—183°:

0·1532 gave 0·2892 CO_2 and 0·897 H_2O. C=51·48; H=6·50.
0·2052 „ 0·0952 AgI. I=25·06.
$C_{21}H_{28}O_4N_2,CH_3I$ requires C=51·36; H=6·03; I=24·7 per cent.

Ethyl 4-p-*Dimethylaminophenyl*-2:6-*dimethylpyridinedicarboxylate.*

A mixture of 37·3 grams of the dihydro-ester and 3·2 grams of sublimed sulphur was gently heated at 150°. The mixture melted, and hydrogen sulphide was rapidly evolved, the heating being continued until the liquid became clear and free from gas bubbles. When cold, the mass solidified, and was dissolved in boiling alcohol, from which it crystallised on cooling. The crude crystals were freed from any uncombined sulphur by dissolving them in excess

of dilute hydrochloric acid and filtering. The ester was precipitated as a white, flocculent mass from the acid solution by means of sodium carbonate solution. It was washed with water and recrystallised from alcohol, and finally from light petroleum. The yield was almost quantitative. The ester is readily soluble in benzene, ether, chloroform, or hot alcohol, sparingly so in warm light petroleum, and melts at 124·5°:

0·1853 gave 7·65 c.c. N_2 (moist) at 3° and 778 mm. N = 7·65.

$C_{21}H_{26}O_4N_2$ requires N = 7·57 per cent.

Hydrolysis.—Fifteen grams of the ester were mixed with 30 grams of potassium hydroxide dissolved in 100 c.c. of alcohol, and the mixture was heated to boiling under a reflux condenser for several hours. On cooling, the *potassium* salt separated out in fine crystals, which were collected and quickly washed with a little absolute alcohol, and dried in a vacuum. A further yield was obtained from the filtrate on concentration. The potassium salt is yellow and very deliquescent in air, changing to a deep yellow mass. It is sparingly soluble in boiling alcohol. The neutral aqueous solution is deep yellow, but the addition of either acid or alkali instantly destroys the colour, which can, however, be restored by the careful neutralisation of the excess of acid or alkali.

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XVII.—*Constituents of the Leaves of* Helinus ovatus.

By JOHN AUGUSTUS GOODSON.

Helinus ovatus, E. Meyer (Nat. Ord. *Rhamnaceae*), is a climbing shrub indigenous to South Africa, where it is found growing on the borders of woods and thickets. No species of this genus, which, according to Oliver ("Flora of Tropical Africa"), is confined to Africa and India, appears to have been examined previously, although the constituents of the genus Rhamnus, from which the order is named, are fairly well known, including as they do such well-known drugs as cascara sagrada and buckthorn.

The results of the present investigation show that *H. ovatus* contains aconitic acid, quercetin, a saponin, and scyllitol. The last-mentioned substance was first isolated from certain plagiostomous fishes, including the spur dogfish, but has since then been

found in a number of plants, such as the acorns of the common oak and the leaves of *Cocos plumosa* and *C. nucifera*.

The occurrence of scyllitol, the second of the two known *meso*-inositols, in these plants is of considerable biological interest in view of the suggestion made by Winterstein, Contardi, and others (compare Posternak, *Compt. rend.*, 1919, **169**, 37) that phytin, which is believed to be the usual organic phosphorus reserve constituent of plants, is a *meso*inositol hexaphosphate.

The material came from Komgha, Cape Province, and was supplied by Mr. I. B. Pole Evans, Chief of the Division of Botany, Union of South Africa, who stated that it is used medicinally by the natives, and is known locally as "soap-plant," since the leaves have the property of yielding a lather when rubbed in the hands with water.

Preliminary Examination.

The leaves contained 9·5 per cent. of moisture and 9·2 per cent. of ash, of which 20·2 per cent. was potash (K_2O), equivalent to 1·8 per cent. in the leaves.

No alkaloid or cyanogenetic glucoside could be detected by the usual reagents.

The finely ground leaves gave the following percentages of extract on exhaustion in a Soxhlet apparatus with solvents in the order named: petroleum (b. p. 35—60°), 2·2; ether, 2·3; chloroform, 2·2; alcohol, 23·0.

Isolation of Ceryl Alcohol.

The petroleum extract consisted of brown, waxy matter, of which about one-third remained undissolved when digested with ether. This was boiled with alcoholic potassium hydroxide solution to remove traces of oil and wax. The residue left after removal of the alcohol was crystallised from ethyl acetate, and then melted at 78°; a specimen of ceryl alcohol melted at 81° in the same bath, and a mixture of the two at 79°. (Found: C = 82·0; H = 14·0. Ceryl alcohol, $C_{26}H_{54}O$ [Henriques, *Ber.*, 1897, **30**, 1415], requires C = 81·6; H = 14·2 per cent.)

The remaining extracts were systematically examined, with results which showed that the quantity of plant available (650 grams) could best be dealt with by extraction with chloroform to remove wax and resinous matter, and then in succession with alcohol and water.

Examination of the Alcoholic Extract.

The bulk of the alcohol was removed, and the resulting syrup set aside for some days, when it deposited a considerable quantity of potassium chloride. The filtrate was poured into about four times its volume of water, and treated successively with lead acetate and basic lead acetate. The lead was removed from the two precipitates and from the filtrate by hydrogen sulphide in the usual manner.

Isolation of Quercetin.

The aqueous solution of the material recovered from the lead acetate precipitate contained a considerable amount of tannin. Extraction with ether removed a small quantity of a yellow substance, probably quercetin (see below). The liquor was then acidified with hydrochloric acid, boiled to hydrolyse glucosides, cooled, and again extracted with ether, the extract yielding a yellow substance crystallising in rosettes of needles. This was recrystallised from a mixture of alcohol and chloroform, and then melted at 309°. On acetylation, it formed matted, colourless needles melting at 195°, and this melting point was not depressed when the substance was mixed with penta-acetylquercetin. The yellow colouring matter is therefore quercetin.

The aqueous solution of the material recovered from the basic lead acetate precipitate also contained tannin, and a small amount of yellow colouring matter, which could not be obtained in a crystalline condition.

The filtrate, after removal of the lead as sulphide, was concentrated and extracted with butyl alcohol, which removed a saponin. The latter was purified by solution in water and precipitation with basic lead acetate, the lead precipitate being decomposed with hydrogen sulphide in the usual manner, and the filtrate evaporated to dryness under diminished pressure. The quantity of saponin obtained was so small that no further purification could be effected. The material frothed strongly in aqueous solution, gave no compound with cholesterol in alcoholic solution, did not reduce Fehling's solution, and was not hæmolytic. It was hydrolysed by boiling with dilute hydrochloric acid, the resulting solution yielding a small amount of apparently crystalline sapogenin on extraction with ether. The residual aqueous solution reduced Fehling's solution strongly, but did not give a crystalline phenylosazone.

The aqueous liquid, after extraction with butyl alcohol, was concentrated under diminished pressure and set aside, when a further

quantity of potassium chloride separated. The filtrate yielded *l*-phenylglucosazone on treatment with phenylhydrazine.

Examination of the Aqueous Extract.

The aqueous extract was treated successively with lead acetate and basic lead acetate, and the two precipitates were collected.

Isolation of Aconitic Acid.

The lead acetate precipitate was suspended in water and decomposed by hydrogen sulphide. The filtrate was concentrated under diminished pressure and extracted with ether, which removed 12·6 grams of a crystalline substance, corresponding with 1·9 per cent. in the leaves.

This, on recrystallisation from water, formed minute prisms melting at 191°, and gave all the reactions of aconitic acid, including that described by Taylor (T., 1919, **115**, 886). (Found: C=41·3, 41·4; H=3·9, 3·6. Aconitic acid, $C_6H_6O_6$, requires C=41·4; H=3·5 per cent.)

Isolation of Scyllitol.

The basic lead acetate precipitate was decomposed in the usual manner, and the filtrate concentrated under diminished pressure, when slightly brown crystals separated. Two crops of the crude substance, amounting to 3 grams and corresponding with 0·46 per cent. in the leaves, were obtained. The product was purified by recrystallisation from hot water, from which it separated in anhydrous, monoclinic rhombs. (Found: C=39·7, 40·1; H=6·8, 6·9. Scyllitol, $C_6H_{12}O_6$, requires C=40·0; H=6·7 per cent.)

The properties of the substance agreed closely with those recorded for scyllitol (J. Müller, *Ber.*, 1907, **40**, 1821, and H. Müller, T., 1907, **91**, 1767; 1912, **101**, 2383). When recrystallised slowly from cold water, it separated in transparent, hexagonal prisms, which, on removal from the solvent, became opaque and friable owing to loss of water of crystallisation. Crystals freed as rapidly as possible from adhering mother liquor lost, on exposure to air, 24·9 per cent. of water. $C_6H_{12}O_6,3H_2O$ requires H_2O=23·1 per cent.

H. Müller noted this change in crystal habit and transparency, but did not establish the fact that it is due to loss of water of crystallisation (T., 1907, **91**, 1772).

When heated, the scyllitol obtained from *H. ovatus* leaves coloured slightly at 300°, darkened considerably at 320°, and melted and effervesced at 353°, as recorded by a mercury thermometer.

J. Müller (*loc. cit.*) gave the solubility of scyllitol in water as about 1 gram in 100 c.c. at 18°; the author finds a solubility of 1·03 grams in 100 grams at 18° for his specimen, whereas H. Müller (*loc. cit.*) gave it as 1·7 grams in 100 c.c. at 15°.

Its identity with scyllitol was confirmed by the preparation of the hexa-acetyl derivative, which melted at 291°. H. Müller (*loc. cit.*) gives 290—291° (corr.). (Found: C=50·1; H=5·6. Hexa-acetylscyllitol, $C_6H_6(C_2H_3O)_6O_6$ requires C=50·0; H=5·6 per cent.)

The filtrate from the lead precipitates, after removal of the lead, contained merely inorganic salts.

In conclusion, the author desires to express his warmest thanks to Dr. Henry for his advice and criticism throughout the course of the work.

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XVIII.—*Contributions to the Chemistry of the Terpenes. Part XIX. Synthesis of a* m-*Menthadiene from* m-iso*Cymene.*

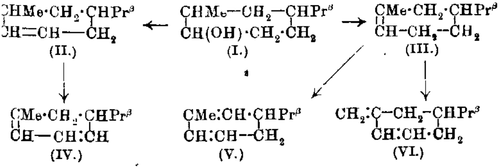
By GEORGE GERALD HENDERSON and THOMAS FREDERICK SMEATON.

SEVERAL menthadienes have been prepared by various synthetic methods, but none that belongs to the meta-series, and may therefore be considered a derivative of *m-iso*cymene, had been synthesised until the problem was successfully attacked by W. H. Perkin, jun., and his collaborators (compare T., 1905, **87**, 1083; 1907, **91**, 480; 1908, **93**, 1876; 1910, **97**, 2129; 1911, **99**, 118). Sylvestrene, carvestrene, and the other meta-menthadienes prepared synthetically by these investigators contain one ethylenic linking in the nucleus and one in a side-chain, hence it appeared desirable to obtain a menthadiene of the meta-series containing two ethylenic linkings in the nucleus in order to compare its properties with those of the corresponding para-menthadienes.

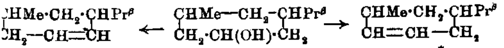
Starting with *m-iso*cymene, obtained by the action of phosphoric oxide on fenchone, we first prepared *m-iso*cymene-6-sulphonic acid

and converted this into the corresponding phenol, 6-hydroxy-*m*-*iso*cymene, by fusion with alkali. The succeeding steps in the process, which was similar to that previously adopted by one of us for the synthesis of menthadienes from thymol and carvacrol respectively (Henderson and Boyd, T., 1911, **99**, 2159; Henderson and Schotz, T., 1912, **101**, 2563), were briefly as follows: (1) Preparation of *m*-menthan-6-ol (1-methyl-3-*iso*propyl*cyclo*hexan-6-ol), $C_{10}H_{19}\cdot OH$, from 6-hydroxy-*m*-*iso*cymene by hydrogenation in the presence of active nickel. (2) Dehydration of the *m*-menthanol by heating with oxalic acid, with the formation of a *m*-menthene (1-methyl-3-*iso*propyl*cyclo*hexene), $C_{10}H_{18}$. (3) Preparation of the *m*-menthene dibromide, $C_{10}H_{18}Br_2$. (4) Conversion of the dibromide into a *m*-menthadiene (1-methyl-3-*iso*propyl*cyclo*hexadiene), $C_{10}H_{16}$, by elimination of two molecular proportions of hydrogen bromide through treatment with alcoholic potassium hydroxide.

It is evident that dehydration of 1-methyl-3-*iso*propyl*cyclo*hexan-6-ol (I) might result in the formation of either 1-methyl-3-*iso*propyl-Δ^5-*cyclo*hexene (II) or 1-methyl-3-*iso*propyl-Δ^6-*cyclo*hexene (III). The dibromide of the former hydrocarbon would yield on treatment with alcoholic potassium hydroxide 1-methyl-3-*iso*propyl-$\Delta^{4:6}$-*cyclo*hexadiene (IV), whilst from the latter either of two isomerides, 1-methyl-3-*iso*propyl-$\Delta^{1:5}$-*cyclo*hexadiene (V) or 1-methylene-3-*iso*propyl-Δ^5-*cyclo*hexadiene (VI), might be produced in a similar manner.



Direct evidence of the constitution of the hydrocarbon, $C_{10}H_{18}$, which we obtained from the *m*-menthanol, is lacking, but its properties are very similar to those of a *m*-menthene which was prepared by Knoevenagel (*Annalen*, 1897, **297**, 169) by heating 1-methyl-3-*iso*propyl*cyclo*hexan-5-ol with phosphoric oxide at 110—130°, and should therefore be either 1-methyl-3-*iso*propyl-Δ^4-*cyclo*hexene or 1-methyl-3-*iso*propyl-Δ^5-*cyclo*hexene:



The physical constants of the two hydrocarbons are as follows:

	B. p.	D.	n_D.	M_D.
H. and S.	167—168°	0·8222	1·45683	45·61
K.	167—168°	0·8197	1·45609	45·67

Comparison of the figures suggests the conclusion that the substances are identical, and therefore that the hydrocarbon which we obtained from 1-methyl-3-*iso*propyl*cyclo*hexan-6-ol is 1-methyl-3-*iso*propyl-Δ^5-*cyclo*hexene (II). If this is the case, the dibromide prepared from it is 5:6-dibromo-1-methyl-3-*iso*propyl*cyclo*hexane, and therefore the hydrocarbon, $C_{10}H_{16}$, which the dibromide yields on treatment with alcoholic potassium hydroxide, is in all probability 1-methyl-3-*iso*propyl-$\Delta^{4:6}$-*cyclo*hexadiene (IV). The following evidence in support of this view may also be quoted. Harries and Antoni (*Annalen*, 1903, **328**, 88) obtained a "dihydrocymene," $C_{10}H_{16}$, by distilling the phosphate of 1:3-diamino-*m*-menthane, which should be either $\Delta^{4:6}$- or $\Delta^{1:5}$-1-methyl-3-*iso*propyl*cyclo*hexadiene. The properties of this hydrocarbon—boiling point 172—174°, $D_{18.5}^{18.5}$ 0·8423, $n_D^{18.5}$ 1·47936—do not correspond at all closely with those of our *m*-menthadiene, which are as follows: boiling point 169—171°, D_{20}^{20} 0·8515, n_D^{20} 1·47270. Apparently, therefore, the latter is not the $\Delta^{1:5}$-isomeride, whilst if the *m*-menthene from which it is derived has the Δ^5-structure, as appears probable, formula VI is also excluded.

Of the three possible formulæ for the menthadiene, there is none in which conjugated double bonds are absent, and, indeed, the fact that it is not capable of uniting additively with more than one molecular proportion of bromine, although containing two ethylenic linkings in its molecule, shows that it has this conjugated structure. Nevertheless, the value found for its molecular refraction was normal, instead of showing an exaltation, as might have been expected. At the same time, it should not be forgotten that, according to Auwers and Eisenlohr (*Ber.*, 1910, **43**, 80), the presence of conjugated ethylenic linkings in a compound can be established with more certainty from consideration of its molecular

$C_{10}H_{16}|\overline{2}$ D_{20}^{20} 0·8515. D_4^{20} 0·8500.

		Molecular refraction.		
Line.	n^{20}.	Found.	Calculated.	Δ.
D	1·47270	44·89	45·24	−0·35
C	1·46964	44·65	44·97	−0·32
G	1·48802	46·21	46·39	−0·18

Molecular dispersion (M_G—M_C).		
Found.	Calculated.	Δ
1·56	1·426	0·134
		=9·4 per cent.

dispersion than from the molecular refraction, and, as shown in the above table, the figures obtained for the *m*-menthadiene confirm the view expressed regarding its structure.

Experimental.

6-*Hydroxy*-m-*isocymene*, $\begin{array}{l}\text{CMe}{=}\text{CH}{-}\text{CPr}^{\beta}\\ \text{C(OH)}{:}\text{CH}{\cdot}\text{CH}\end{array}$.

m-*iso*Cymene (1-methyl-3-*iso*propylbenzene) was prepared from fenchone by treatment with phosphoric oxide, according to Wallach's method (*Annalen*, 1893, **275**, 158), and converted into 6-hydroxy-*m*-*iso*cymene by the process described by Kelbe (*Annalen*, 1881, **210**, 30), with certain modifications. On warming with concentrated sulphuric acid, *m*-*iso*cymene yielded readily a mixture of *m*-*iso*cymene-6-sulphonic acid and *m*-*iso*cymene-4-sulphonic acid, the latter only in small proportions. The sulphonic acids were converted into their barium salts in the usual way, and the salt of the 4-acid, which is more readily soluble in water, was separated from the sparingly soluble salt of the 6-acid. The potassium salt of the 6-acid was obtained by heating the barium salt with a concentrated aqueous solution of potassium carbonate, and purified by crystallisation from water, from which it separates in lustrous plates. Finally, the potassium salt was fused with six times its weight of potassium hydroxide, the fusion dissolved in water, the solution acidified, and the 6-hydroxy-*m*-*iso*cymene distilled over in a current of steam. From the distillate it was separated, partly by means of a tap funnel and partly by extraction with ether, dried, and distilled (b. p. 231°). It is a colourless, refractive liquid, the vapour of which has a very irritating effect on the lungs.

1-*Methyl*-3-iso*propyl*cyclo*hexan*-6-*ol* (I).

The 6-hydroxy-*m*-*iso*cymene was converted into 1-methyl-3-*iso*propyl*cyclo*hexan-6-ol by treatment with hydrogen in the presence of active nickel. In order to obtain the nickel in an active form, the hydroxide of the metal was precipitated by the addition of potassium hydroxide to a solution of the pure nitrate, the precipitate washed exhaustively with water, formed into a paste by admixture of granules of pumice, and dried. The greater part of a long combustion tube was filled with the mixture, and the oxide of nickel reduced with pure hydrogen at 280°. The 6-hydroxy-*m*-*iso*cymene was placed in a boat in the front part of the tube, which was maintained at 170—180° while a steady stream of carefully

purified hydrogen was passed through. The hydrogenation product distilled slowly into the receiver as a colourless liquid. Attempts to crystallise the compound from various solvents, or by cooling, having proved unsuccessful, it was purified by distillation under diminished pressure.

1-*Methyl*-3-iso*propyl*cyclo*hexan*-6-*ol* is a colourless, somewhat viscous liquid with a pleasant odour. It is very sparingly soluble in water and readily so in alcohol or ether. Its physical constants are as follows: boiling point 119—121°/28 mm., D_{20}^{20} 0·9156, n_D^{20} 1·46659, M_D found 47·30, calc. 47·55.

1-*Methyl*-3-iso*propyl*-Δ^5-cyclo*hexene* (II).

In order to effect dehydration, the purified 1-methyl-3-*iso*propyl-*cyclo*hexan-6-ol was mixed with about twice its weight of finely powdered anhydrous oxalic acid and boiled for several days in a flask provided with an air condenser until the process appeared to be completed. The contents of the flask were distilled in a current of steam, when a clear, oily liquid passed over and floated on the surface of the aqueous layer. The distillate was saturated with ammonium sulphate and extracted with ether, the ethereal extract washed with water and dried over anhydrous calcium chloride, and the ether removed by distillation. The residual liquid was distilled, and two fractions were collected, the larger one boiling at 165—185° and the other at 185—205°. The latter was set aside for further treatment with oxalic acid, and the fraction which boiled at 165—185° was redistilled over sodium until a product of constant boiling point was obtained. 1-*Methyl*-3-iso*propyl*-Δ^5-cyclo*hexene* is a colourless, mobile liquid with an agreeable odour. Its boiling point is 167—168°/760 mm., D_{20}^{20} 0·8222, n_D 1·45683. M_D found 45·61, calc. for $C_{10}H_{18}|^{-}$ 45·39. It is unsaturated, immediately decolorising solutions of potassium permanganate and of bromine.

5 : 6-*Dibromo*-1-*methyl*-3-iso*propyl*cyclo*hexane*, $\begin{matrix}\text{CHMe—CH}_2\text{—CHPr}^\beta \\ \text{CHBr·CHBr·CH}_2\end{matrix}$

A cooled solution of bromine (1 mol.) in glacial acetic acid was added gradually to a solution of the *m*-menthene (1 mol.) in the same solvent, cooled with ice-water, and stirred continuously. After addition of the bromine, the solution was left for half an hour and then poured into ice-water. The *dibromo*-derivative settled down as a heavy, oily liquid, almost colourless, which was washed with water until free from acetic acid, and used for the next operation without further purification

1-*Methyl*-3-iso*propyl*-$\Delta^{4:6}$-cyclo*hexadiene* (IV).

The dibromo-derivative was boiled for several hours under a reflux condenser with an excess of alcoholic potassium hydroxide until no further separation of potassium bromide took place. The mixture was then distilled in a current of steam, and the oily distillate separated from the water with the aid of light petroleum. The extract was washed with water and dried over anhydrous potassium carbonate, and the petroleum then distilled off. The liquid which remained was fractionally distilled over sodium in an atmosphere of dry hydrogen; no signs of decomposition were observed during the process, and the distillate was perfectly colourless. After several fractionations, a product of constant boiling point was obtained.

1-*Methyl*-3-iso*propyl*-$\Delta^{4:6}$-cyclo*hexadiene* ($\Delta^{4:6}$-m-*menthadiene*) is a colourless, limpid liquid with an agreeable odour. It boils at 169—171°/760 mm., and has D_{20}^{20} 0·8515, n_D^{20} 1·47270, M_D found 44·89, calc. for $C_{10}H_{16}|\overline{2}$ 45·24. The hydrocarbon is unsaturated, at once reducing an alkaline solution of potassium permanganate, but is not capable of combining additively with more than one molecular proportion of bromine. With sulphuric acid, it gives a red, with sulphuric acid and alcohol a reddish-brown, and with acetic anhydride and sulphuric acid a violet, coloration. From the results of the determination of its physical constants, shortly after purification and again after an interval of seven days, it evidently undergoes change, probably polymerisation, on keeping. Thus the following results were obtained with a specimen which had been set aside for a week after purification: D_{20}^{20} 0·8614, n_D^{20} 1·47437, M_D found 44·44. The *m*-menthadiene appears, in fact, to behave in a similar way to *cyclo*pentadiene (compare Auwers and Eisenlohr, *loc. cit.*).

We take this opportunity of expressing our gratitude to Mr. W. G. Birrell for valuable assistance in the experimental part of the work, and to the Research Fund Committee of the Carnegie Trust for a grant in aid of the expenses.

UNIVERSITY OF GLASGOW. [*Received, January* 15*th*, 1920.]

XIX.—*The Effect of a Change in Temperature on the Colour Changes of Methyl-orange and on the Accuracy of Titrations.*

By Henry Thomas Tizard and John Reginald Harvey Whiston

In a former paper (T., 1910, **97**, 2477), one of us gave the results of quantitative measurements of the depth of colour of solutions of methyl-orange containing varying concentrations of hydrogen ions. The results could be quantitatively accounted for on the simple theory that methyl-orange was a (pseudo-) acid of a strength of about $4 \cdot 2 \times 10^{-4}$ at about 25°, and that the depth of colour of the red (undissociated) form of the acid was 18·8 times that of the yellow dissociated form or acidic ion in solutions of the same strength. The calculation of the dissociation constant depends directly on the latter measurement, for (see previous paper) if α is the degree of dissociation of the indicator acid and C_0 the depth of colour of the undissociated molecule compared to that of the dissociated molecule as unity, the colour of a solution containing a fraction α of the acid in the dissociated form is:

$$C = C_0(1 - \alpha) + \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the concentration of the hydrions in the solution is given by

$$C_H = K \cdot \frac{1 - \alpha}{\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If C_0 and C are measured, α can be calculated from (1) and K from (2). A mistake in the value of C_0 of course alters the calculated value of K.

The results recorded in the present paper agree at 25° very well with the older measurements in not too acid solutions. When more acid is present, they are consistently lower. This may be partly due to the fact that a different sample of methyl-orange was used, but it is more likely that the depth of colour in the more strongly acid (red) solutions was previously overestimated. This would mean that the value of K at 25°, calculated in the previous paper, was too high; present measurements give $3 \cdot 8 \times 10^{-4}$ at 25° instead of $4 \cdot 25 \times 10^{-4}$. It is, naturally, difficult to compare accurately the depths of colour of solutions which differ in tint, even though the difference is very slight, as in the present case.

The determination of the concentration of hydrions in aqueous solutions by means of "indicators" has been frequently used during

the last few years. It has been generally assumed that the effect of temperature on the depth of colour of solutions containing methyl-orange was practically negligible. It was pointed out, however, in a paper read before the British Association in 1912 that this was probably not the case. There seems very little doubt that indicators in general use are pseudo-acids or bases. Now, the strength of pseudo-acids usually increases considerably with the temperature; in other words, their dissociation constants have a very high temperature-coefficient. The sensitiveness of an indicator depends, however, directly on its dissociation constant; if the constant increases, the indicator will become less sensitive to hydrions, and therefore the depth of colour in a solution of any definite hydrion concentration (within the range of sensitiveness) will diminish. A qualitative experiment showing this effect is as follows: if an $N/200$-solution of acetic acid containing methyl-orange is heated, the colour of the solution will change from orange to yellow, and increase again on cooling.

Since no quantitative experiments have been made on the effect of temperature on the changes of indicators, it was thought advisable to determine the depth of colour of methyl-orange in solutions of varying acidity at three different temperatures. The measurements were carried out exactly as before with a modified Donnan colorimeter constructed by Köhler in Leipzig. The colorimeter tubes were jacketed outside with tubes, through which a stream of water could be passed. The temperature of the solutions in the colorimeter tubes was thus kept constant by siphoning water through the jacketed tubes from a reservoir kept at the desired temperature. The temperature inside the tubes was (at the higher temperatures) a few degrees lower than that of the bath, but could easily be kept constant within 1° during the series of experiments.

The solutions of varying hydrion concentration were made by mixing known quantities of equivalent solutions of ammonia and acetic acid. These two substances are of practically the same strength, and, further, their strength, and especially that of acetic acid, alters only slightly with the temperature, as the following numbers taken from Lundén's tables show:

	18°	25°	40°
Ammonia	1·4	1·77	$1{\cdot}87\times10^{-5}$
Acetic acid	1·82	1·86	$1{\cdot}81\times10^{-5}$

Now if we add z c.c. of ammonia to (say) 10 c.c. of an equivalent solution of acetic acid, then if z is less than 10, we have a solution containing $(10-z)$ equivalents of acid and z equivalents of salt (ammonium acetate), which may be considered to be completely

dissociated in dilute solutions. Then if V is the (unknown) dilution, the concentration of hydrions is given by

$K_a \times$ (concentration of acetic acid) = (concentration of acetion) $\times$ (concentration of hydrion).

Hence

$$C_H = \frac{K_a \times (10 - z)}{z} = \frac{1 \cdot 8 \times 10^{-5} (10 - z)}{z},$$

and is independent of V, provided this is neither too small nor too large, and also of the temperature, since K_a alters so little with the temperature. This is by far the easiest way of preparing solutions of any definite concentration of hydrions between 10^{-3} and 10^{-7} (the neutral point).

It is not necessary to know the strengths of the acid and alkaline solutions absolutely so long as their relative strengths are known accurately. For this purpose, it is best to titrate the acid solution directly against standard baryta, using phenolphthalein as indicator, and the ammonia solution, using methyl-red as indicator, against a solution of hydrochloric acid which itself has been titrated against the same baryta solution.

The effect of temperature on the "end-colours" of methyl-orange, that is, on the depth of colour in highly acid and in neutral or alkaline solutions ($C_H < 10^{-7}$), is practically zero. No difference in the depth of colour of the red acid form could be detected when the temperature ranged from 10° to 40°; this means that whatever is the form of the undissociated acid which imparts the distinctive red colour to the solution, its concentration is altered very little with rise of temperature. The depth of colour of the yellow (alkaline) solution, which one may suppose to contain only the ion, $N(CH_3)_2 \cdot C_6H_4 \cdot N \colon N \cdot C_6H_4 \cdot SO_3'$, appeared to increase slightly when the temperature was raised from 10° to 40°, but the increase is within the unavoidable errors of measurement at these temperatures. The mean of many experiments gave 17·5 as the molecular colour of the undissociated acid, taking that of the yellow dissociated form as unity.

The depths of colour of solutions containing concentrations of hydrions within the limits of sensitiveness are given in the following tables; from the results, the following values for the (apparent) dissociation constant of the indicator were obtained:

Temperature......	15°	24°	37°
K	2·7	3·7	$5 \cdot 2 \times 10^{-4}$

The values for the depth of colour in the various solutions, calculated from these numbers, are given in the third column of the

ables. The results previously obtained for 25° are included in he table for 24°. The agreement is very satisfactory, except in the more acid solutions; it should be remembered that the former results were all obtained in dilute solutions of hydrochloric acid.

Temperature, 15°; $K=2\cdot7\times10^{-4}$; $C_0=17\cdot5$.

Concentration of hydrions.	Colour (observed).	Colour (calculated).
$1\cdot3\times10^{-6}$	1·10	1·12
5·9 ,,	1·33	1·35
$2\cdot8\times10^{-5}$	2·57	2·55
7·0 ,,	4·45	4·38
$1\cdot6\times10^{-4}$	7·00	7·14
3·34 ,,	10·0	10·1
5·0 ,,	11·7	11·7
$1\cdot0\times10^{-3}$	14·3	14·0
2·0 ,,	15·3	15·5
3·7 ,,	16·0	16·4
$1\cdot0\times10^{-2}$	17·1	17·1
$1\cdot0\times10^{-1}$	17·8	17·5

Temperature, 24°; $K=3\cdot7\times10^{-4}$; $C_0=17\cdot5$.

Concentration of hydrion.	Colour (observed).	Colour (calculated).	Previous measurements at 25°.*
$0\cdot16\times10^{-4}$	1·66	1·68	1·65
0·365 ,,	2·50	2·48	2·41
0·91 ,,	4·28	4·25	4·13
2·15 ,,	7·10	7·06	7·03
5·0 ,,	10·4	10·5	10·6
$3\cdot7\times10^{-3}$	15·7	16·0	—
10^{-1} (N/10-HCl)	17·4	17·5	18·3

* T., 1910, **97**, 2477.

Temperature, 37°; $K=5\cdot2\times10^{-4}$; $C_0=17\cdot5$.

Concentration of hydrion.	Colour (observed).	Colour (calculated).
$0\cdot28\times10^{-4}$	1·90	1·84
0·535 ,,	2·61	2·54
1·58 ,,	4·54	4·84
2·15 ,,	5·60	5·82
5·0 ,,	9·20	9·10
$1\cdot0\times10^{-3}$	11·6	11·4
2·0 ,,	14·0	14·1
3·7 ,,	15·4	15·5
$1\cdot0\times10^{-2}$	16·3	16·7
10^{-1}	17·5	17·4

In the diagram, depths of colour are plotted against concentration of hydrions. The three curves represent the results at the three temperatures chosen; it will be seen that the effect of raising the temperature is to shift the colour curve to the left. The dissociation constant increases linearly with the temperature; extra-

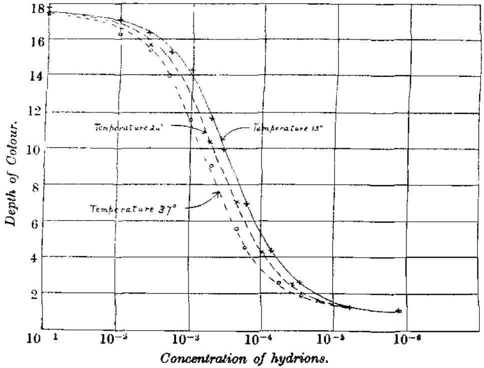
polation gives the following values for the temperatures 10°, 25°, and 40°:

Temperature	10°	25°	40°
Dissociation constant	2·1	3·8	$5{\cdot}5\times10^{-4}$

It can be easily shown (see equation 2) from these results that the concentration of hydrion necessary to produce any definite depth of colour is doubled by raising the temperature from 15° to 40°.

Discussion of Results.

The very great temperature-coefficient of the dissociation constant of methyl-orange may be taken as strong evidence of the truth of



the modern theory that this indicator is a pseudo-acid. No other case in the literature of the subject can be found of an acid of this order of strength ($K=10^{-4}$) increasing in strength appreciably within these limits of temperature. At the same time, it is necessary to reconcile this conclusion with the fact that the red colour of the undissociated acid form of the indicator does not change in depth when the temperature is altered. The obvious explanation of the high temperature-coefficient of the dissociation constant of pseudo-acids is that the equilibrium between the pseudo- and true acid forms of the acid, which we may express by the formula

$$HXO \rightleftarrows HOX,$$

alters considerably with the temperature. If this is true of methyl-orange, why does not the colour alter? The following seems to be a satisfactory explanation of this difficulty. Methyl-orange, or rather helianthin, is a sulphonic acid. If it were not a pseudo-acid we should therefore expect it to be a strong acid, comparable with sulphuric acid, with a dissociation constant of about 1. Assuming this, we may say that since its dissociation constant is actually found to be of the order 3×10^{-4} (at the ordinary temperature), then the undissociated form of the acid must be an equilibrium mixture consisting almost entirely of the red pseudo-form (or forms) HXO, whilst only a fraction, 3×10^{-4}, of it is in the yellow, "true acid form" HOX. Increase in temperature to 40° means that this fraction is increased to $5{\cdot}5 \times 10^{-4}$, without appreciably altering the proportion in the pseudo-acid form. Hence the colour remains practically unchanged.

Since the depth of colour of methyl-orange in a solution containing an $N/5000$-concentration of hydrogen ions ($C_H = 10^{-3\cdot7}$) is 5·45 at 40° and 9·1 at 10°—an increase of 65 per cent. for a fall in temperature of 30°—it is clear that if the methyl-orange method is employed for determining quantitatively the concentration of hydrions in a solution, it is important to keep the temperature constant during the measurements. The effect of a change in temperature on the accuracy of an ordinary titration is, however, only very slight. The concentration of hydrogen ions in a solution of a salt made up of a weak base and strong acid is approximately

$$\sqrt{\frac{K_w}{K_b V}}$$

where K_w and K_b are the dissociation constants of water and the base respectively, and $\frac{1}{V}$ is the concentration of the salt in mols. per litre.

The effect of the increase of the dissociation constant of methyl-orange with the temperature is that the concentration of hydrions "indicated" is greater the higher the temperature. Since, however, $\sqrt{\frac{K_w}{K_b}}$ also increases with the temperature, the two effects tend to cancel each other, and the accuracy of the titration is not impaired. Taking collidine ($K_b = 1{\cdot}6 \times 10^{-7}$ at 18° and 3×10^{-7} at 40°) as an example of a base for the titration of which methyl-orange is a suitable indicator, the concentration of hydrions at the "equivalent" point, if $V = 20$, is 4×10^{-5} at 18° and 7×10^{-5} at 40°. The dissociation constant of methyl-orange increases from

3×10^{-4} to $5 \cdot 5 \times 10^{-4}$ for this range of temperature, and the depth of colour of methyl-orange in solutions of the above concentration would be 3·0 at 18° and 2·8 at 40° respectively, a difference which is, of course, negligible. The accuracy of a titration in such cases depends mainly on quite other factors, chief of which is the effect of a small excess of acid or base on the hydrolysis of the salt, and this depends only on the strength of the acid or base in question, and not at all on the indicator. In other words, a change in temperature, within reasonable limits, can never necessitate a change of indicator.

We are much indebted to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the cost of the colorimeter.

OXFORD. [*Received, January 6th*, 1920.]

XX.—*The Rate of Decomposition of Malonic Acid.*

By CYRIL NORMAN HINSHELWOOD.

THE experiments described in this paper were carried out with the object of obtaining information bearing upon recent views on chemical reactivity. The view of Marcelliu and of Rice, that a molecule reacts when its energy exceeds the mean energy corresponding with the temperature of the system, was coupled by Lewis (T., 1916, **109**, 796) with the hypothesis that the rate of a unimolecular reaction is proportional to the density of infra-red radiation of the frequency absorbable by the system. By introducing a term derived from Planck's equation into the ordinary mass-action equation, Lewis obtained $E = Nh\nu$, where E/N = critical increment for one single molecule, h = Planck's constant, and ν = the frequency of the absorbed infra-red radiation. A detailed account of the radiation theory is given by Perrin (*Ann. Phys.*, 1919, [ix], **11**, 5).

In connexion with Rice's view, it is interesting to make measurements of the rate of unimolecular reaction in a system the energy content of which can be varied at constant temperature, for example, to compare the reactivity of a solid system with that of the supercooled liquid at the same temperature. If, moreover, a marked difference in reactivity is found between the two systems, the radiation hypothesis would lead one to expect a difference in their infra-red properties. Naturally, a unimolecular reaction

must be selected for investigation, in order that heterogeneity may not complicate the problem.

Malonic acid was chosen for experiment, since at moderately high temperatures it undergoes a unimolecular decomposition into volatile products, namely, carbon dioxide and acetic acid. The first part of the work was to measure the rate of decomposition of molten malonic acid above its melting point and the supercooled liquid below the melting point, and to compare the values of the velocity constant k for the supercooled liquid with the corresponding values for the solid. If a large difference existed, it would be worth while looking for a difference in the infra-red properties of the acid in the two states. Actually, a well-marked difference is found in the rates, as the results will show.

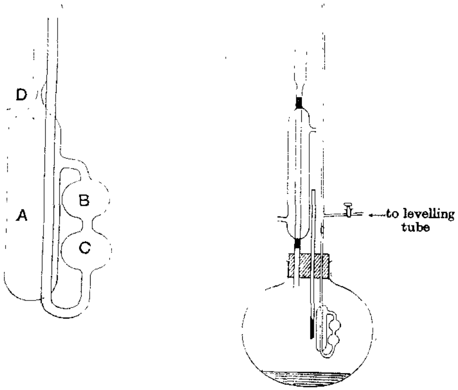
The rate of decomposition of malonic acid was measured in glacial acetic acid solution by Lindner (*Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, 945), and found to be unimolecular, but the rate of decomposition of the acid alone does not appear to have been determined.

The acid was prepared in the ordinary way from chloroacetic acid, and was twice recrystallised from pure ether. Two preparations melted at 133·9° (corr.) and 134·3° respectively, the melting point being difficult to determine with great precision owing to incipient decomposition. (Values given in the literature vary from 131° to 134°.)

The apparatus for measuring the rate of decomposition manometrically is shown in Fig. 1. *A* is a glass bulb of about 20 c.c. capacity, into which small quantities of malonic acid, usually about 20 milligrams, are introduced. *C* is a reservoir containing mercury for the manometer, whilst *B* acts as a trap, preventing mercury from *C* from entering the bulb *A*. When the acid has been introduced into *A* and the mercury into *C*, the apparatus is sealed off at *D*. The decomposition bulb was heated either in a vapour bath or in an electrically heated aud controlled oil thermostat. The arrangement of the apparatus when the vapour-bath was used is shown in the right-hand sketch of Fig. 1. The large globe contains a liquid of suitable boiling point (bromobenzene, propylene bromide, tetrachloroethane, xylene, amyl acetate, acetic anhydride, ethylene dibromide, amyl alcohol, and glacial acetic acid were employed). The decomposition bulb is joined by means of pressure tubing to the long manometer tube, which communicates by the tap to a levelling tube containing mercury. The method of taking readings was as follows. When a constant temperature had been attained, the mercury had usually risen to a point not far below the T-piece leading to the levelling tube.

The tap was opened and the pressure increased until the mercury in the decomposition vessel reached a fixed mark between the bulbs *B* and *C*. As decomposition proceeded, the pressure required to bring the contents of *A* and *B* back to constant volume increased and measured the progress of the reaction. When connexion was first made between the manometer and the levelling tube, air bubbles were usually introduced. These were easily removed by pushing a long piece of fine capillary tube down the manometer. The thermometers were compared with a standard thermometer, and the bulb was always placed close to the acid in *A*. Care was

FIG. 1



taken that the condenser runnings did not touch the thermometer or the bulb *A*. For the shorter experiments, this arrangement was very satisfactory, but for longer experiments, owing to barometric changes, the electrically controlled thermostat was preferable. The heating arrangement in this consisted of about a metre of "nichrome" wire with a resistance of 50 ohms wound on a mica frame and immersed directly in the oil-bath. It was connected with the 100-volt main in parallel with the motor driving the stirrer. The regulator was filled with quinoline. Auxiliary heating was provided by a Bunsen burner. The mean temperature remained very constant, but it was impossible to suppress a rapid

periodic fluctuation. As this amounted to about ±0·3° with a two-minute period, and this arrangement was only used with experiments lasting many hours, the regular variations were of no account. The manometric readings were corrected for barometric changes.

At temperatures above the melting point, the amount of drying of the acid does not appear to influence the result, nor were divergences shown by two separate preparations of malonic acid.

The following table gives the results obtained at different temperatures for the fused acid above its melting point and for the supercooled acid. It was found possible to keep it supercooled at 125°.

TABLE I.

t = time in minutes; p = pressure in mm.; p_∞ = final pressure;

$$k = \frac{1}{t}\log_{10}\frac{p_\infty}{(p_\infty - p)}.$$

Temperature 153·6°.			Temperature 136·4°.			Temperature 129·4°. Liquid supercooled.		
t.	*p.*	*k.*	*t.*	*p.*	*k.*	*t.*	*p.*	*k.*
6·5	57	0·0265	10	37·0	0·00568	20	70	0·00263
10·0	85	0·0290	15	53·0	0·00559	35	117	0·00262
14·5	108	0·0288	20	67·0	0·00545	52	167	0·00265
29·0	152	0·0304	27	87·0	0·00547	68	216	0·00276
100·0	175		35	108·0	0·00549	82	251	0·00278
Final	175		45	131·0	0·00549	100	292	0·00280
Mean value of k = 0·0287			56	155·0	0·00558	120	332	0·00281
			64	171·0	0·00566	135	361	0·00285
			100	223·5	0·00585	166	418	0·00298
			Final	302·0		195	462	0·00305
			Mean value of k = 0·00558			Final	*615*	
								Mean 0·00279

Other values obtained were:

Temperature	153·2°	143·5°	142·3°	134·2°	133·6	125·9°
Mean value of k......	0·0279	0·0099	0·00947	0·00456	0·00397	0·00204*

* Liquid supercooled.

In calculating k, the variation in the association of the acetic acid vapour was not taken into account.

In Fig. 2, the decimal logarithm of K $(=k \times 10^3)$ is plotted against the temperature. There is no regular deviation from a straight line. By the method of least squares, the following expression is deduced:

$$\log_{10}K = 0{\cdot}04157(T-100) - 0{\cdot}7778 \quad . \quad . \quad . \quad . \quad (1)$$

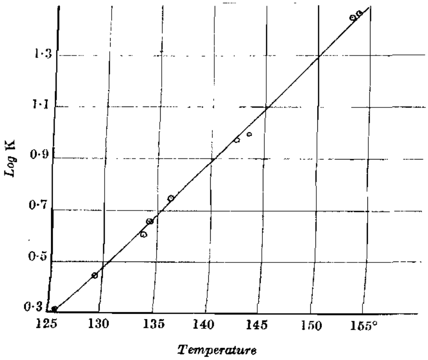
where T = temperature.

The following table shows the degree of validity of the expression:

Temperature.	*K* (calculated).	*K* (found).
153·6°	28·2	28·7
153·2	27·2	27·9
143·5	10·7	9·9
142·3	9·56	9·47
136·4	5·44	5·58
134·2	4·41	4·56
133·6	4·16	3·97
129·4	2·78	2·79
125·9	1·99	2·04

It may therefore be employed to calculate *K* for the supercooled liquid at points not far outside the range of temperature actually

FIG. 2.



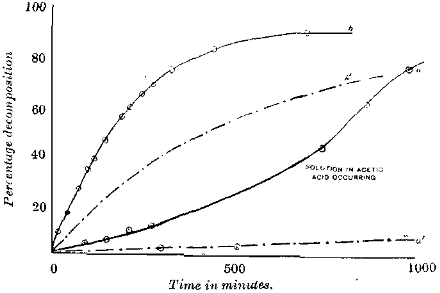
observed, so that comparison may be made between the behaviour of the supercooled liquid and that of the solid.

The solid is much less reactive than the supercooled liquid, the value of *k* being of quite a different order of magnitude. It must be stated at the outset, however, that *k* for the solid is a much less well-defined constant and difficult to measure accurately, since it appears to be greatly influenced by traces of moisture and mode of preparation of the sample, which conditions are quite unimportant in the case of the liquid.

It was hoped that by the use of small quantities and by work-

ing at temperatures above the boiling point of acetic acid, disturbances due to the condensation of acetic acid would be avoided. This was only partly realised. It was possible to measure the rate of decomposition of the solid acid over a considerable range, but not over the whole range, since at a certain point, depending on the temperature and the relation between the weight of malonic acid and the volume of the bulb, acetic acid began to condense and dissolve the solid. The very slow rate of reaction then increased, and the nature of the curve changed. *Fig. 3 illustrates* this point. The curves *a* and *a′* show the rate of decomposition of the solid at 125·9° and 116·5° respectively. Curve *b* shows the rate of decomposition of the supercooled liquid at 125·9° as actually

FIG. 3.



a. Solid at 125·9° *b. Supercooled liquid at* 125·9° *(experimental curve).*
a′. ,, 116·5° *b′.* ,, ,, 116·5° *(calculated).*

measured, whilst curve *b′* shows that of the supercooled liquid at 116·5°, calculated from the value of *k* given by equation (1). The rapid increase in rate of reaction when the acetic acid begins to condense and dissolve the malonic acid is observable in curve *a*. An exactly similar phenomenon was later observed in the case of *a′*, but the scale of the diagram does not allow it to be shown. It will be seen, however, from the figures given below.

Values of *k* for the solid deduced from experiments of this sort would not be trustworthy. The following method was therefore adopted. Weighed quantities of malonic acid—from five to ten times the amounts used in the above experiments—were heated in vessels of accurately known volume. The initial rate of decom-

Temperature 125·9°.

(a) Solid.

t.	p expressed as percentage of final pressure.
90	4·7
150	6·9
210	10·8
270	12·6
750	48·7
870	68·7
990	84·8
1110	93·4
1230	97·9
1350	99·5
2500	100·0

(b) Supercooled liquid.

t.	p expressed as percentage of final pressure.
22	9·1
26	11·4
44	17·9
60	23·3
75	28·2
103	37·3
121	42·0
149	50·3
170	55·4
195	60·9
216	65·3
250	71·0
279	75·4
327	81·8
445	92·0
511	97·1
705	100·0
1365	100·0

Temperature 116·5°.

(a) Solid.

t.	p expressed as percentage of final pressure.	
240	1·2	
300	2·4	
511	4·05	
1090	9·5	
1210	10·7	
1390	12·8	
1575	15·0	
1725	17·0	Solution in the acetic acid accompanied by a rapid increase in rate.
1948	19·55	
2558	29·4	
2808	34·7	
3030	40 3	
3200	45·5	
3372	53·2	
4001	89·3	
4291	96·1	
4686	99·0	
5500	100·0	

(b)′ Liquid supercooled. Calculated from value $k = 0{\cdot}00081$ given by equation (1).

t.	p.
119	20
274	40
491	60
863	80

position, conveniently expressed in c.c. of gas at *N.T.P.* per gram of malonic acid, could thus be measured without any reference to the later stages of the reaction. Little trouble was caused by acetic acid in these early stages. Slight acceleration

was still sometimes observed, due, presumably, to the retention of acetic acid by the solid. It was in all cases slight and easily eliminated by expressing the rate as a function of the form $ax+b$ (where x=the amount of decomposition). a being quite small, approaching zero, b, the true initial rate, was obtained without appreciable error. In order to arrive at k from the initial rates thus measured without making any assumptions as to the state of association of acetic acid vapour, etc., an exactly similar experiment was carried out with the liquid acid, for which k was known. In this way, the factor was directly obtained for converting "initial rates" into velocity constants.

Temperature 132·2°. Molten acid, k=0·00364.

Time in minutes.	C.c. reduced to N.T.P. (assuming gas laws); calculated on 1 gram of malonic acid.
2·0	4·5
7·0	14·0
12·0	23·8
19·5	38·1

that is, initial rate = 1·92 c.c. per gram per minute.

An initial rate of 1·92 c.c. per gram per minute thus corresponds with k=0·00364.

The following rates were determined with the carefully dried solid from the same preparation, and although the actual values cannot be regarded as indicating more than the order, for the reasons given above, they are of some interest.

TABLE II.

Temperature 126·3°.

Minutes. t.	C.c. per gram of malonic acid. x.
30	4·9
90	12·4
120	16·4
150	19·7
210	27·3
270	38·4
351	57·2

$$\left(\frac{dx}{dt}\right)_0 = 0·134$$

$$\text{whence } k = \frac{0·134 \times 0·00364}{1·92} = 0·00025$$

Temperature 125·5°.

t.	x.
90	12·0
180	20·8
300	35·7
450	54·7

$$\left(\frac{dx}{dt}\right)_0 = 0·117$$

$$\text{whence } k = \frac{0·117 \times 0·00364}{1·92} = 0·00022$$

TABLE II. (*continued*).

Temperature 121·2°.

Minutes. t.	C.c. per grain of malonic acid. x.
60	1·8
126	3·5
186	5·4
253	7·4
604	20·6

$$\left(\frac{dx}{dt}\right)_0 = 0{\cdot}026$$

$$\text{whence } k = \frac{0{\cdot}026 \times 0{\cdot}00364}{1{\cdot}92} = 0{\cdot}000049$$

Temperature 117·3°

t.	x.
60	1·9
120	2·8
180	4·1
265	6·5
373	9·7
465	12·8

$$\left(\frac{dx}{dt}\right)_0 = 0{\cdot}0215$$

$$\text{whence } k = \frac{0{\cdot}0215 \times 0{\cdot}00364}{1{\cdot}92} = 0{\cdot}000041$$

Temperature 110·8°.

t.	x.
150	1·04
240	1·76
42?	3·39

$$\left(\frac{dx}{dt}\right)_0 = 0{\cdot}0065$$

$$\text{whence } k = \frac{0{\cdot}0065 \times 0{\cdot}00364}{1{\cdot}92} = 0{\cdot}000012$$

Temperature.	k for the solid acid.	k for the super-cooled liquid.	Ratio.
126·3°	0·00025	0·00207	8
125·5	0·00022	0·00192	9
Rejected (121·2	0·000049	0·00127	26)
117·3	0·000041	0·00087	21
110·8	0·000012	0·00047	39

From the increase in the ratio in the last column, as the temperature falls it appears that the temperature-coefficient for the solid is much greater than that for the liquid measured over the same range, so that, as the temperature decreases, the difference between the reactivity in the two states becomes more and more pronounced. One would expect the statistical energy–distribution curve of the solid to approach that of the liquid in the neighbourhood of the melting point. In criticism, it must be remarked that any impurities, such as occluded solvent, would give rise to increasing amounts of liquid phase as the temperature approached the melting point. This would lead to an unduly large temperature-coefficient, since the variation, due solely to increase in temperature, would be superimposed on that due to the increased amount of liquid phase.

In view of the fact that the malonic acid was carefully purified and melted at the correct temperature, it is almost impossible that this would account for more than a small fraction of the increased temperature-coefficient. Otherwise visible amounts of liquid should have been observed at 125°, whilst actually no trace was noticed. Nevertheless, the criticism must be borne in mind until further experiments are made.

The discussion of the bearing these results may have on the radiation hypothesis may be left until the study of the infra-red properties is completed.

In conclusion, I have pleasure in thanking Mr. H. B. Hartley and Mr. D. H. Nagel for much help and advice.

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Oxford. [*Received, December 18th, 1919.*]

85 AGRICUL

XXI.—*Some Observations on the Action of Coal upon a Photographic Plate.*

By Eric Sinkinson.

This paper is the outcome of an attempt to discover what constituent of the coal substance is responsible for its well-known action on a photographic plate in the dark.

W. J. Russell (*Proc. Roy. Soc.*, 1908, [*B*], **80**, 376) found (1) that coal and resin (among other substances), when placed on or near a sensitised plate in the dark for varying periods of time, reacted in such a way that, on developing the plate, an image was obtained, (2) that such action is dependent on the presence of air or oxygen, and (3) that it also requires direct contact between coal and the plate. The interposition of glass, mica, or metal between the two will prevent it.

Clark, Wheeler, and Platt (T., 1913, **103**, 1713) employed the method to show that cellulose has no action on a photographic plate, and from this concluded that the portion soluble in pyridine contained the resinic constituent of the coal substance, because it acted intensely. By treating the part soluble in pyridine with chloroform, the extract obtained was found to produce an image on a plate, whilst the residue gave no image. They concluded, therefore,

that the chloroform extract contained the resinic, and the residues the cellulosic, portions of the coal substance. The results of the experiments recorded in this paper throw doubt on this conclusion. Stopes has also shown that, of what she has termed the three visible ingredients of a banded, bituminous coal, namely, durain, clarain, and vitrain (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 470), the last-named has the strongest action on a photographic plate.

EXPERIMENTAL.

As already stated, the action of coal on a photographic plate depends on the presence of oxygen. Thus, if a piece of coal is placed on a plate in a light-tight box and all the air displaced by nitrogen, no action will result, even after a period of twenty-four hours at 40°. Further, a small quantity of water vapour will prevent any action, even in the presence of air. Moreover, if the box is exhausted, no image can be obtained.

In order to decide whether the said effect of oxygen is caused by some actual oxidation of the coal substance or by some specific action on the plate, it was found that light will affect a plate *enveloped in nitrogen apparently to the same extent as in air.* Therefore it would appear that the presence of oxygen is essential to the action of coal, but not to that of light.

A series of experiments was also carried out on a Brodsworth "soft" coal in order to find whether the continued exposure of it in an atmosphere of oxygen at 40° would reduce its power of affecting a photographic plate. The samples were exposed to oxygen in both blue- and red-tinted bottles, and also to strong white light, in order to see whether the rate of absorption was altered. This was not so; even in bottles covered with "Berlin black" the rate of absorption of oxygen was approximately the same as in plain white bottles. The coal, when completely saturated with oxygen, was placed on a photographic plate side by side with an untreated sample. The latter undoubtedly gave the more intense image on development of the plate. This would indicate that the absorption of oxygen is part of the mechanism of the action of coal on a photographic plate.

Russell tentatively suggested that the production of hydrogen peroxide may be responsible for the change in the photographic plate, because the effect can be imitated by a suitable application of it to a plate.

So far, it has been impossible to find a test sufficiently delicate or decisive to confirm his suggestions. Daylight in the fiftieth of a second can bring about a result far greater than that of coal

acting for a period of twelve hours. The minute quantity of substance in the sensitive medium of the plate involved in the reaction renders the difficulty of detecting a cause obvious.

It seemed first of all necessary to inquire into the stability at high temperatures of the constituents of the coal that can react on a photographic plate in the dark, and the following describes how this information was obtained.

A.

A sample of Mauvers Main coal (containing 5·7 per cent. of water) was ground and dried at 105° in the usual way, and 15 grams were introduced into a distillation tube closed at one end. The open end was closed by a stopper, through which was fixed a delivery tube connected with an aspirator filled with a mixture of glycerol and water; a manometer was inserted to indicate the slightly reduced pressure maintained throughout the carbonisation.

The distillation tube and connexions were exhausted, and heat was applied by a gas furnace, the temperature of which was measured by a platinum-rhodium–platinum thermo-couple. The first experiment was made at 300°, and this was considered complete when no more volatile matters were expelled, that is, when gas ceased to be evolved; this took about six hours.

Similar experiments were made at 500°, 700°, and 1000°, the last being in a porcelain tube.

The residue was removed from the tubes in turn, ground to a coarse powder, and placed on a photographic plate in small heaps covered by inverted porcelain crucibles.

The plate* was enclosed in a light-tight box and warmed in an incubator to 40° for twenty-four hours. It was then developed, with the result shown in the illustration.

(*a*) The dry sample gives the most intense image, the undried being slightly less in comparison.

* An investigation was made to determine which type and speed of plate was most suitable for this work. In order to do this a large piece of coal was selected and smaller pieces of similar structure were broken from it and the surfaces rubbed flat. These were placed each on a different plate in a light-tight box which was warmed in an incubator for twenty-four hours. The plates used were Ilford "Monarch," Ordinary, Process, Chromatic, Panchromatic, Super Speed Ortho, and *X*-Ray. The Chromatic or Panchromatic gave no image. The Ordinary gave a poor image, Super Speed Ortho gave a fairly good one, but the best was obtained with an *X*-Ray plate. The only difference apparently between an *X*-Ray plate and the other type is that it has a slightly thicker film. Accordingly, the *X*-Ray type of plate was chosen for this work.

(*b*) The sample heated to 300° has much less effect; at 500° there is only very slight evidence of any action.

(*c*) At 700° and 1000° no action can be detected.

The black ring, so evident in the dried and undried original samples, is undoubtedly produced by the "vapour" pouring from the coal, as noted both by Russell and Wheeler under similar conditions.

B.

It became necessary at this stage to study the action of coal heated to temperatures in the region of 500°; for the first series of experiments, which were repeated several times with different coals, establish the fact that the reactive principle is still present in the coal at this temperature.

Accordingly, the working temperatures chosen were 450°, 500°, and 550°. In order to make the investigation more comprehensive, coals of widely divergent origin were carbonised at these temperatures under exactly similar conditions, as follows:

(1) Two Spanish (coking and non-coking) bituminous coals of similar composition (kindly placed at my disposal by Prof. W. A. Bone), and

(2) Hamstead coal (Birmingham) and the ingredients of it, namely, durain, clarain, and vitrain, investigated by Stopes (*loc. cit.*).*

The two Spanish and the Hamstead coals, together with the ingredients of the last, were pulverised and dried. The six were then carbonised at the successive temperatures 450°, 500°, and 550°, as follows.

A weighed sample of each was placed in one of six separate hard glass tubes closed at one end, so as to form a retort, the open end being closed by a rubber stopper carrying a delivery tube. The six delivery tubes were connected to a common main, and so to a gasholder filled with glycerol and water. The whole of the gaseous products then entered the gasholder, which served to maintain an even reduction of pressure in all the distillation tubes.

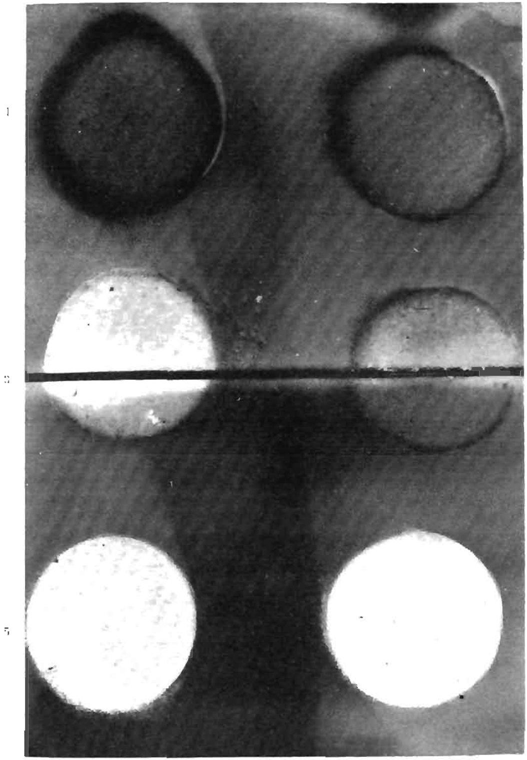
The tubes were heated together in an electric muffle furnace at the desired temperatures until all the volatile matter had been removed, for six hours as before. The temperature was measured by a calibrated platinum-rhodium–platinum thermo-couple.

* "Durain" is the equivalent of "dull" hard coal or the "Mattkohle" of the Germans.

"Clarain" and "Vitrain" are the equivalent of "bright" or glance coal, the "Glanzkohle" of the Germans.

"Vitrain" gives a conchoidal fracture, brilliant in appearance.

Fig. 1.



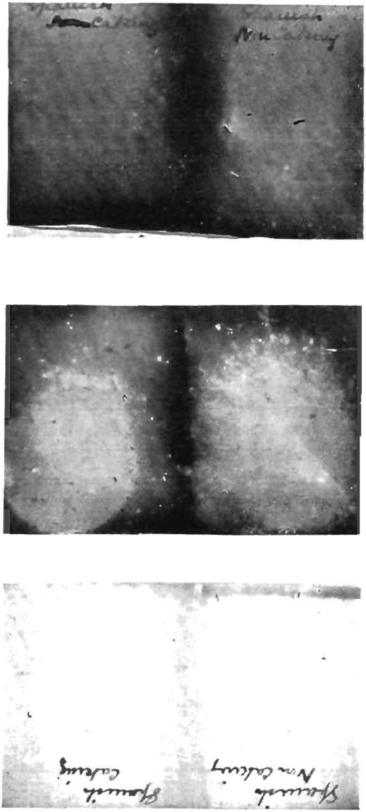
1. *Dry coal before carbonising.*
2. *Wet coal before carbonising.*
3. *Carbonised at 500°.*
4. *Carbonised at 300°.*
5. *Carbonised at 1000°.*
6. *Carbonised at 700°.*

[*To face page* 168.

FIG. 2.

1 2

450° 500° 550°



1. *Spanish coking.* 2. *Spanish non-coking.*

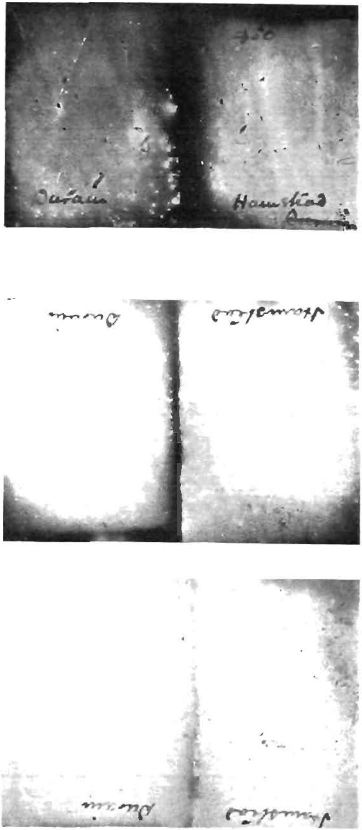
Fig. 3.

3 4

450°

500°

550°



3. *Durain.* 4. *Hamstead.*

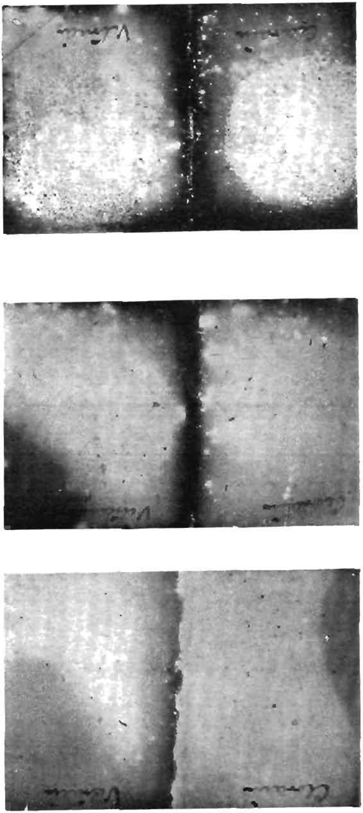
FIG. 4.

5 6

450°

500°

550°



5. *Vitrain.* 6. *Clarain.*

In this manner, the coals were carbonised under exactly comparable conditions at the three selected temperatures.

The residues were coarsely powdered and placed in turn on photographic plates, six heaps on each plate. The plates were contained in cardboard boxes, and these were placed in a specially constructed light-tight box, so that the carbonised products of the coals could be subjected to strictly comparable conditions.

The box was placed in an incubator, maintained at 37°, for three weeks, after which time the plates were removed and developed together at the same temperature. In order to give a positive effect on the prints, the plates were "printed" on to other plates, 'rom which the illustrations shown were taken.

Discussion of Results.

The coals and separate ingredients carbonised at 450° give images on a photographic plate in the dark, but at 500° the effects are not so intense, although in some cases, such as Hamstead and durain, there is a decided diminution of effect.

For a carbonising temperature of 550° the effect is not perceptible, except perhaps in the case of the Hamstead, which is just perceptible. The critical point lies between 500° and 550°.

At 450° vitrain undoubtedly gives relatively the most intense image; at 500° this dies away rapidly.

Clarain is next in intensity, and also diminishes at 500°. Durain is less intense than either vitrain or clarain at a carbonising temperature of 450°, and dies away rapidly at 500°.

The order of these intensities bears out what Stopes found for these ingredients at the ordinary temperature.

The Hamstead coal carbonised at 450° gives the same order of intensity as durain, perhaps a little less marked, and this effect dies away rapidly at 500°, but is still faintly perceptible at 550°.

The Spanish coking and non-coking coal give similar degrees of intensity at 450°, but, unlike the others, the effect persists more strongly at 500°. They show, however, no trace of effect at 550°.

Russell's failure to obtain an image on a photographic plate from a coal which had been heated at 200° for twenty-four hours, a period far beyond that required to expel completely the volatile matters at that temperature, raises an interesting point in connexion with the destruction of the coking properties of coal by continued heating. De Marsilly in 1857 found that all coking coals lost their property of forming coke after being heated at 300° for some time. Anderson explains this by assuming the presence of a "resinoid" substance responsible for the coherence

of a coking coal. If, then, it be true that a resinic substance is responsible for the coking property of a coking coal, which can be destroyed by continued heating, also that the reactivity to a photographic plate can be traced to the same principle, the cause is explained.

In the present series of experiments, the coking coals, namely, the Spanish, carbonised at 500°, gave quite a good coke after heating for six hours, a time sufficiently long to expel all the volatile matters at that temperature.

Since resin has a similar effect to coal on a plate, and coal is known to contain resin, it might be considered reasonable to conclude that resin in coal is the activating agent towards the plate.

This conclusion was contradicted when, during the course of an unpublished research in conjunction with Prof. Bone, the author found that the pure resin, or, more precisely, the resen portion of resin, produces no effect on a photographic plate in the dark.

Clark, Wheeler, and Platt obtained an intense effect from the pyridine extract of a coal, and this is believed to contain, among other substances, the resinic constituents. It would seem, therefore, that in the pyridine extract is to be found the ingredieut causing the action on a photographic plate, and the remaining constituents of this extract, other than the resen, should be responsible for this effect.

This question is now under investigation.

In conclusion, the author desires to record his best thanks to Prof. W. A. Bone for his interest in the work; to Drs. Wheeler and Stopes for the loan of the specimens of Hamstead coal; to Dr. Stopes, in addition, for the specimens of durain, clarain, and vitrain; and to Mr. Ernest Bury, M.Sc., for grantiug him certain facilities at the Skinningrove Iron Company's works for the prosecution of the work during July and August, 1919.

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XXII.—*The Sorption of Hydrogen by Palladium at Low Temperatures.*

By JAMES BRIERLEY FIRTH.

IN a previous communication (Holt, Edgar, and Firth, *Zeitsch. physikal. Chem.*, 1913, **82**, 513), a summary of the views held on the sorption of hydrogen by palladium is given. The view is also advanced that sorption takes place through an amorphous metallic phase, which acts as a carrier for the hydrogen to the crystalline metal. Further, the activity of the palladium is determined by the presence of the amorphous variety on the film. This amorphous variety is metastable, hence the decay in activity is due to the disappearance of this variety. It can be reproduced on the surface by heating to a red heat in a vacuum or in hydrogen, or by oxidising the surface and then reducing the oxide in hydrogen; the activity of the palladium can therefore usually be renewed by one of these methods.

Andrew and Holt (*Proc. Roy. Soc.*, 1913, [*A*], **89**, 170), from a consideration of the heating and cooling curves in hydrogen, find further evidence of two states of the metal. The rapid occlusion of this gas is attributed to the presence of the amorphous variety. In absence of the amorphous film, the palladium may be quite passive in the cold, or at any rate the sorption may be exceedingly slow. At temperatures above 100°, no matter whether the palladium be originally passive or active, a rapid occlusion of a small amount of hydrogen invariably takes place. At temperatures above 150°, all forms of palladium have equal affinity for the gas.

Halla (*Zeitsch. physikal. Chem.*, 1914, **86**, 496), in a criticism of the above two communications, expresses the view that the palladium, characterised by Graham as inactive, is not really inactive, but apparently so owing to a film of occluded oxygen on the surface.

Holt (*Proc. Roy. Soc.*, 1914, [*A*], **90**, 226), from a study of the rate of solution of hydrogen by palladium, draws the following conclusion: "The rate of solution of hydrogen by palladium is not a simple function of the concentration of the gas in the metal. The rate curves consist of two portions (except in the case of palladium black), which have been interpreted as referring to solution in two different forms of the metal. The smooth rate curve for palladium black is taken to mean complete absence of one of these forms."

Paal and Amberger (*Ber.*, 1905, **38**, 1394) determined the

occlusion of hydrogen by palladium black at $-10°$ by heating in hydrogen at 110° and cooling to $-10°$, and found the amount of hydrogen considerably increased.

Gutbier, Gebhardt, and Ottenstein (*Ber.*, 1913, **46**, 1453), by the same method as Paal and Amberger, determined the occlusion down to $-50°$, and found occlusion considerably increased with diminution of temperature.

Sieverts (*Zeitsch. physikal. Chem.*, 1914, **88**, 105), in two communications, shows that from 100° to 1500° occlusion diminishes with rise of temperature. Palladium black at 137° occludes larger volumes than foil at the same temperature. At higher temperatures, amorphous and crystalline palladium occlude hydrogen by solution merely; at lower temperatures, amorphous palladium takes up further quantities by adsorption.

S. Schmidt (*Ann. Physik*, 1904, [iv], **13**, 747) finds that at temperatures between 140° and 300° the volume of hydrogen occluded increases with fall of temperature; below 140°, the results were not concordant.

Partington (*Trans. Faraday Soc.*, 1919, **14**, 259) calculates the heat of dissociation of hydrogen from the dissociation pressures of "palladium hydride" given by Troost and Hautefeuille (*Compt. rend.*, 1874, **78**, 686), and obtains the value 4568 gram-calories, which is in close agreement with the experimental value, 4672, obtained by Mond, Ramsay, and Shields (*Trans. Roy. Soc.*, 1898, [*A*], **191**, 105).

The object of the experiments described in the present communication was to study the activity of palladium at low temperatures, in particular at the temperature of liquid air and at 0°, and, so far as possible, to determine the equilibrium pressures under these conditions. Previous investigators have apparently had as their object the maximum volumes which can be occluded by palladium at low temperatures, and have started occlusion at some higher temperature and cooled the palladium to the required temperature (compare Paal and Amberger). In the present work, the maximum occlusion attainable was not given any special consideration. It is the opinion of the author that the existence of at least two allotropic modifications of palladium has already been proved, namely, α-, or amorphous, palladium, and β-, or crystalline, palladium. The α-form is highly active, and is responsible for rapid occlusion at temperatures up to about 150°; it is further capable of acting as a carrier to the β-variety, which may be completely passive or moderately active, according to conditions of temperature.

The term "adsorption" is used to indicate rapid occlusion of

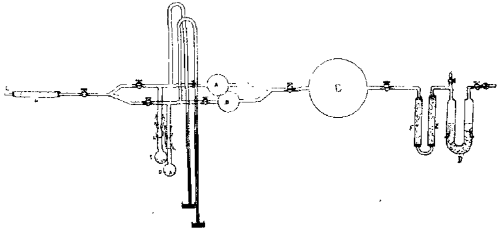
hydrogen, that is, where diffusion is not a determinable factor. "Absorption" denotes the slower process, in which the rate of diffusion or solution is a determinable factor. "Sorption" is used as a collective term, and includes adsorption and absorption (compare McBain, *Phil. Mag.*, 1909, [vi], **18**, 916).

Experimental.

The apparatus used is indicated in Fig. 1. Bulbs I and II are of quartz, and contain the palladium, each bulb being connected to a separate manometer. *A* and *B* are reservoir bulbs of about 250 c.c. capacity. *C* is a large bulb of about 1 litre capacity used as a reservoir for hydrogen.

The hydrogen was prepared by the electrolysis of barium hydr-

Fig. 1.



oxide in U-tube *D*, and dried by passing through tubes *E* and *F* containing phosphoric oxide.

The apparatus can be exhausted through tube *G*, which is connected with a Toepler pump, *H* being a drying tube containing phosphoric oxide. Bulbs I and II were immersed in cooling baths to *h* and *h'* respectively.

The palladium foil used in these experiments was from the same sample as that employed in the previous research (Holt, Edgar, and Firth, *Zeitsch. physikal. Chem.*, 1913, **82**, 513).

Bulb I contained 1·0075 grams of palladium foil, and bulb II 1·0100 grams.

(*a*) The palladium, as received, was exposed in bulb I to hydrogen at the ordinary temperature (16·8°) and atmospheric pressure (758 mm.). Bulb II was immersed in liquid air, and then hydrogen admitted to atmospheric pressure.

The manometer remained at zero for more than four hours, no hydrogen being sorbed in either case, *that is, the palladium was inactive.*

(*b*) The palladium in bulbs I and II was heated to a red heat in a vacuum for about five minutes, bulb II was then immersed in liquid air, and bulb I kept at the ordinary temperature (16·4°), both samples being exposed to hydrogen under atmospheric pressure (757 mm.). After four hours, the liquid air was removed, and both samples were left in contact with hydrogen overnight at the ordinary temperature. Next morning, the amount of hydrogen sorbed by 1 volume of palladium (volumes of hydrogen corrected to N.T.P.) was as follows:

Bulb I, 10 vols. Bulb II, 0 vol.

(*c*) Experiment (*b*) was repeated, with the following result:

Bulb I, 12 vols. Bulb II, 3 vols. (approx.).

(*d*) The palladium in bulbs I and II was heated to a red heat in a vacuum for one hour, and then exposed to hydrogen exactly as in (*b*). Result:

Bulb I, 14 vols. Bulb II, 3·5 vols.

From the above results, it appears that heating in a vacuum has failed to activate the palladium to any great degree, and, further, the sample immersed in liquid air always gave a lower result.

(*e*) The palladium from each bulb was then transferred to a crucible and heated in air for two hours in order to coat it with a thin film of oxide, the palladium then being returned to the bulbs. The bulbs were exhausted, bulb II was immersed in liquid air and then exposed to hydrogen at atmospheric pressure, and bulb I exposed to hydrogen at the ordinary temperature (15·8°) and atmospheric pressure (758 mm.). Result:

BULB I.

Hydrogen rapidly sorbed:

10 mins. ...	... 240 vols.
11 mins. ...	... 432 ,,
Next morning ...	684 ,,

BULB II.

No hydrogen sorbed while in liquid air (6 hours). After 6 hours, liquid-air bath removed, no sorption took place for 25 minutes, then sorption began, slowly at first, with increasing rapidity.

30 mins. after removal of liquid air	10 vols.
35 ,, ,, ,,	37 ,,
40 ,, ,, ,,	108 ,,
45 ,, ,, ,,	227 ,,
Next morning	525 ,,

(*f*) The palladium in bulb II was oxidised by heating in air for two hours and the bulb exhausted. About 1 c.c. of hydrogen was admitted to reduce the oxide, and the bulb again exhausted. It was then immersed in liquid air and hydrogen admitted to atmo-

spheric pressure. No sorption took place during a period of six hours, when the liquid air was removed and the palladium allowed to attain the ordinary temperature. After thirty-two minutes, sorption began, and finally 742 volumes were sorbed.

(*g*) The palladium in bulb I was oxidised by heating in air for two hours, and then exposed to hydrogen under atmospheric pressure. Hydrogen was taken up immediately, and, after 377 volumes had been sorbed, the bulb was immersed in liquid air, with the result that sorption ceased; after three hours, the liquid-air bath was removed and the palladium allowed to attain the ordinary temperature. After ten minutes, hydrogen was rapidly sorbed, and finally 798 volumes were taken up.

After expelling the hydrogen from the palladium in each case at a dull red heat, and when the palladium had again reached the ordinary temperature, the samples were immediately exposed to hydrogen, but no sorption took place, even after a period of two days, therefore the palladium had become inactive.

From the above experiments, it would appear (*a*) that "active" palladium is "inactive" at liquid-air temperature; (*b*) that the immersion in liquid air tends to retard the activity at the ordinary temperature, and to some extent to lower the sorption value.

The film of oxide on the palladium did not appear to have been removed while in the liquid-air bath in experiment (*e*).

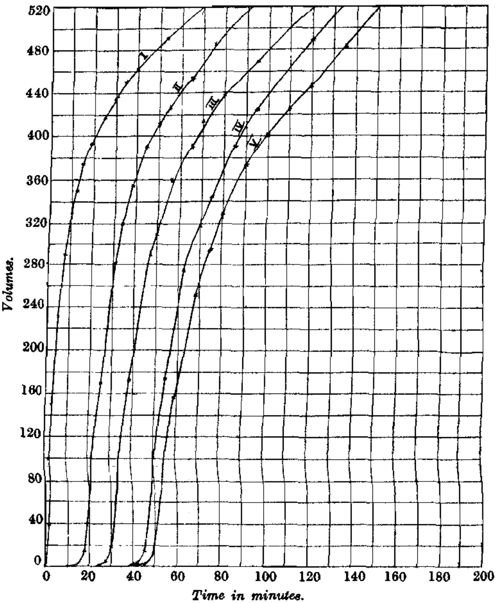
In order to determine more fully the influence of liquid air on the activity of palladium, the following experiments were made.

Before each experiment, the palladium was activated by heating it in air for two hours, thus becoming coated with a thin film of oxide. The only difference between each experiment was in the length of time of cooling at liquid-air temperature. After the removal of the liquid air, the bulb was dried externally, and, after a lapse of five minutes, exposed to hydrogen at the ordinary temperature and atmospheric pressure. The rates of sorption were then observed, and the results obtained are shown graphically in Fig. 2. The first curve is the normal curve, the palladium having been exposed to hydrogen at the ordinary temperature (16·5°) without any previous cooling. Curves II, III, IV, and V represent the results after previous cooling in liquid air for one, three, six, and nine hours respectively. On comparing the results, it appears that there is a definite "lag" in the activity of the palladium after cooling in liquid air, and, further, the longer the periods of cooling the longer is the "lag." When the sorption does commence, it is very slow at first, but soon becomes normal.

From the foregoing experiments, it would appear that not only is the palladium, which is active at the ordinary temperature,

inactive at liquid-air temperature, but on returning to the ordinary temperature it is temporarily passive to hydrogen, the period of passivity depending on the duration of cooling. It is clear that this passive condition of palladium is different from the variety

FIG. 2.

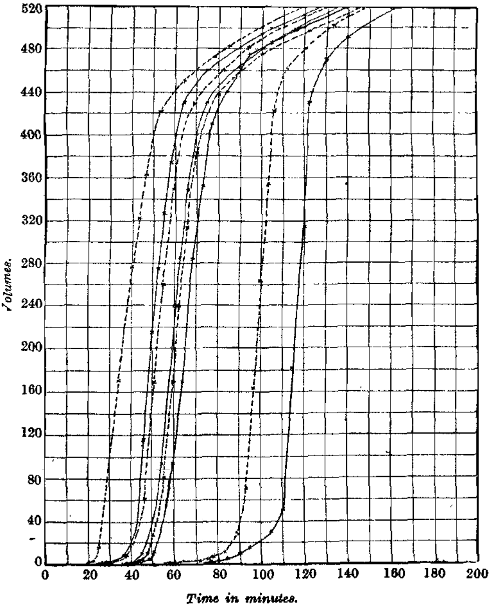


which is "dead," irrespective of the time of contact with hydrogen, since it returns to normal activity.

In order to delay the transformation from the "passive" to the "active" condition, another series of experiments was made which differs from the series just described only in the temperature at which the palladium was exposed to hydrogen. In this series, the

palladium was placed in a bath of melting ice immediately on removal of the liquid-air bath. These experiments were carried out in bulb I, and simultaneously a second series in bulb II was carried out in which the palladium was cooled in an ice-bath for

Fig. 3.



the same period as bulb I was cooled in liquid air before exposing to hydrogen at 0°. The results obtained in both cases are shown graphically in Fig. 3. Commencing from the left of the diagram, the continuous curves represent the results after cooling with liquid

air for one, three, six, and nine hours, respectively, prior to exposure to hydrogen at 0°.

The broken curves represent the results after cooling at 0° for one, three, six, and nine hours, respectively, prior to exposure to hydrogen at 0°.

From these results, it would appear that not only does the ice-hath increase the period of passivity of the palladium after cooling in liquid air, but also the palladium becomes passive after cooling at 0°. After a time, however, sorption begins, even at 0°; the rate is very slow at first, but finally reaches a normal one.

In all cases, the period of "lag" increases with time of previous cooling.

Furtber experiments were made in which additional precautions were taken and any disturbing factors eliminated so far as possible.

It was observed that several of the pieces of foil were very much pitted by repeated use, so fresh pieces of foil, each about 0·25 sq. cm., with smooth surfaces were selected.

1·0105 Grams of foil were oxidised by heating in air for four hours in order to obtain a uniform film, and then carefully introduced into bulb I, and again heated in air to oxidise any portion which had been accidentally rubbed while being transferred to the quartz bulb. The bulb was exhausted and cooled in a double ice-bath for twenty-four hours, after which period hydrogen was carefully admitted. Care was taken to eliminate any vibration by avoiding unnecessary movement in the vicinity of the apparatus and by not disturbing the apparatus during the replenishing of the ice-baths.

By taking all conceivable care, a permanent period of inactivity seemed to be obtained. The palladium remained inactive for forty-eight hours, after which the activity under ordinary conditions was tested by the removal of the ice-bath. The palladium remained inactive for a further period of 145 minutes, after which sorption began, the rate being slow at first. The results were as follows:

145 mins.	... ...	0·0 vol.
175 „	... ...	10·3 vols.
190 „	... ...	98·6 „
195 „	... ...	187·8 „
Final	... ...	778·5 vols. (excluding initial adsorption)

Several attempts were made to repeat this experiment, and four consecutive experiments gave the following periods of passivity: (*a*) 5 hours; (*b*) 3 hours 37 minutes; (*c*) 48 hours; (*d*) 7 hours 11 minutes. In experiment (*c*), the passivity was considered permanent, and the ice-bath was removed at the end of two days. The final volumes sorbed in the above cases were: (*a*) 810 vols.;

(*b*) 805 vols.; (*c*) 803 vols.; (*d*) 792 vols.* Why sorption commenced in experiments (*a*), (*b*), and (*d*) is not quite clear from the present information, but possibly some local disturbance occurred.

In all experiments at 0°, the oxide appeared to be reduced immediately on admission of hydrogen. In order to test this point, a further series of experiments was performed in which the oxide was first reduced by admitting 1 c.c. of hydrogen before cooling to 0°, exhausting as completely as possible, and cooling at 0° for twelve hours before admitting hydrogen. The periods of passivity in five experiments were: (*a*) 7 hours 10 minutes; (*b*) 45 minutes; (*c*) 26 hours 19 minutes; (*d*) 15 hours 42 minutes; (*e*) 11 hours 17 minutes.

The volumes sorbed were: (*a*) 812 vols.; (*b*) 819 vols.; (*c*) 807 vols.; (*d*) 798 vols.; (*e*) 817 vols.*

The palladium in bulb I was heated in air for two days; the oxide film was reduced by admitting 1 c.c. of hydrogen, and then allowed to remain for two days at the ordinary temperature in a vacuum. Hydrogen was then admitted at the ordinary temperature and atmospheric pressure (757 mm.). The gas was slowly sorbed, and, after twenty-four hours, only 227 volumes of gas had been occluded. Hence the α-variety had been largely transformed into the β-variety.

In order to test further the reduction of palladium oxide at 0°, 0·5 gram of palladium oxide was cooled in bulb I for one hour, and then exposed to hydrogen. The oxide was instantly reduced.

In the experiments previously described, the hydrogen was admitted until atmospheric pressure was reached, an operation which only took a few seconds, but rapid adsorption (if any) would take place during the admission of the hydrogen and would not be recorded on the manometer. In order to determine the extent of such adsorption, the following experiments were made.

(*a*) 1·0150 Grams of inactive palladium were exposed to hydrogen at 16·7° and atmospheric pressure (758 mm.). The bulb was immersed in liquid air, when the manometer rose rapidly, and then remained steady. Hydrogen was next admitted until the pressure was atmospheric. The bulb was then opened to the pump and the liquid-air bath removed, the hydrogen being pumped off and measured. After correcting for adsorption by the wall of the quartz bulb (from a blank experiment), it was found that 143·9 volumes of hydrogen had been adsorbed.

(*b*) The palladium was rendered active by oxidising the film in air. It was then cooled to liquid-air temperature and exposed to

*Excluding the initial adsorption which took place immediately on admitting hydrogen.

hydrogen under atmospheric pressure. The volume of gas adsorbed was measured as before. On attaining the ordinary temperature, some of the gas passed into the interior of the metal, and the last traces of hydrogen were removed by heating to a dull red heat. The volume of the gas corresponded with an adsorption of 317 volumes.

(*c*) Similar experiments at 0° gave adsorptions of 17·5 vols. and 45 vols. respectively. In the case of active palladium, measurement was made after fifteen minutes and before any apparent diffusion into the interior of the metal had taken place.

(*d*) Palladium activated by oxidising in air was saturated with hydrogen at the ordinary temperature and atmospheric pressure, and approximately 815 vols. were taken up. The palladium was *then cooled in liquid air, the hydrogen being maintained under* atmospheric pressure. The total gas was measured as before, the last portion of hydrogen being evolved by heating to a dull red heat. Hydrogen corresponding with a sorption of 1156 vols. was collected, being an addition of 341 vols., due to cooling.

(*e*) A similar experiment at 0° gave an increase of 74·5 vols. over that sorbed at the ordinary temperature.

(*f*) Active palladium was saturated witb hydrogen at liquid-air temperature, as described in experiment (*d*), and as much as possible was removed while at liquid-air temperature. After pumping off the gas for six hours, 415 vols. of gas were removed, and the manometer registered a vacuum. After remaining for one hour, no change in pressure was observed, and it was not possible to pump off measurable quantities of gas at this temperature within a reasonable time. On removing the liquid-air bath and heating to redness, 727 vols. of gas were evolved.

(*g*) Active palladium was cooled in a freezing mixture at −11° in a vacuum for thirty minutes, and then exposed to hydrogen under atmospheric pressure. No absorption took place after twelve hours' contact, and 117 vols. of hydrogen were adsorbed.

(*h*) Active palladium saturated with hydrogen at 15·7°, then cooled in a freezing mixture to −11°, gave a total sorption of 987 vols.

Determination of Equilibrium Pressures at 0°.

The palladium was oxidised by heating in air for thirty minutes, the bulb immersed in an ice-bath, and, after ten minutes, exposed to successive quantities of hydrogen, equilibrium being attained after each addition.

On the first addition there was a lag of twenty-three minutes,

on the second addition a lag of three minutes, but on each subsequent addition sorption began immediately.

The results are given in table I, and are shown graphically by curve AB in Fig. 4.

TABLE I.

C.c. of gas occluded by 1 vol. of metal	55·8	116·2	782·5	260·6	336·8
Equilibrium pressure in mm.	6·5	8·4	10·5	12·75	14·8
$\sqrt{P_{AB}}$	—	2·92	3·24	3·57	3·87
P_{AC}*	—	1·9	3·0	3·2	3·7
P^2_{AB}/V	—	0·6082	0·6057	0·6243	0·6501
C.c. of gas occluded by 1 vol. of metal	405·4	460·4	544·3	571·6	613·5
Equilibrium pressure in mm.	26·5	36·3	72·8	87·5	105·9
$\sqrt{P_{AB}}$	5·15	6·02	8·53	9·35	—
P_{AC}*	4·6	5·6	8·4	9·6	—
P^2_{AB}/V	1·734	2·828	9·7	13·4	—

* From graph AC Fig. 4.

The hydrogen was then removed in successive stages and the "equilibrium" pressure determined after each removal. The results are given in table II and shown graphically by curve AC in Fig. 4.

TABLE II.

C.c. of gas occluded by 1 vol. of metal	613·5	597·1	576·6	525·2	452·1	376·5	297·9	212·1	163·1	94·8
Equilibrium pressure in mm.	105·9	18·2	10·2	7·6	5·8	4·4	3·5	3·1	2·5	1·5

It will be observed that for the same concentration of hydrogen there are two "equilibrium" pressures, and a similar result was obtained by Holt, Edgar, and Firth (*Zeitsch. physikal. Chem.*, 1913, **82**, 513). In this case, the difference in the two cases is not so marked. The curve AB at 100° showed no horizontal portion, and was not in any way similar to AC, whereas at 0° the results give similar curves.

The curve AB may be taken to represent the equilibrium pressures of "adsorbed" hydrogen, and AC (lower portion) that of the "absorbed" hydrogen.

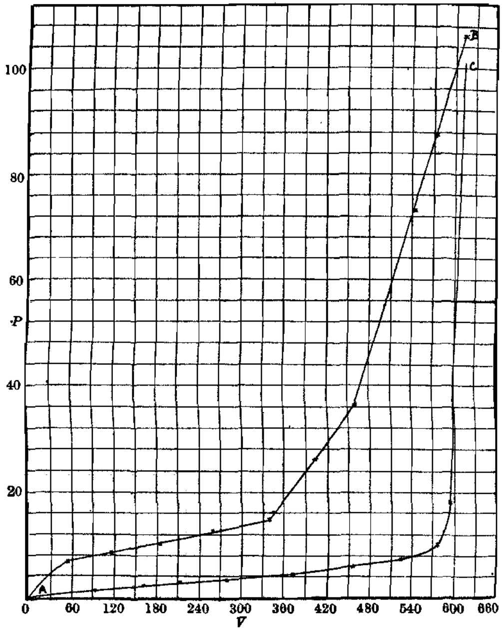
The relationship between the two sets of results may be approximately represented thus:

$$V\sqrt{P_{AB}} = VP_{AC} \quad \text{or} \quad \sqrt{P_{AB}} = P_{AC}.$$

In table I values for P^2_{AB}/V are given, and the results show that

below 400 vols. the value approaches a constant; similarly, P^4_{AC}/V would approach the same constant. These results would indicate a difference in molecular complexity between the hydrogen in the surface layer and that in the interior of the metal.

FIG. 4.



Conclusions.

The inactivity of the palladium used in the first three experiments cannot be reasonably attributed to the presence of a film of oxygen, as suggested by Halla, since in the second and third experi-

ments a small amount of hydrogen was occluded and expelled by heat, which would remove the last traces of oxygen.

Sieverts and others have shown that at high temperatures the occlusion of hydrogen is one of simple solution, or "absorption," whilst the experiments herein described show that at low temperatures "adsorption" only takes place. The limiting temperature for diffusion into the interior is probably about 0°. Where the palladium has been previously saturated with hydrogen and cooled to a temperature below 0°, the increase in volume is due to adsorption.

The conclusions may be briefly stated thus:

(*a*) Below 0°, adsorption only.

(*b*) 0—150°, adsorption followed by absorption.

(*c*) Above 150°, absorption only.

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[*Received, December* 12*th*, 1919.]

XXIII.—*The Interaction of Chlorine and Marsh Gas under the Influence of Light. The Conversion of Methyl Chloride to Methyl Alcohol and Methyl Acetate.*

By JOHN REGINALD HARVEY WHISTON.

THE photochemical interaction of chlorine and methane has been the subject of several investigations. Frankland (*Quart. Journ. Chem. Soc.*, 1850, **3**, 338), who first studied the reaction, believed that the principal product was methyl chloride when equal volumes of the two gases were taken, and principally methylene dichloride when the volume of the chlorine was twice that of the methane. Berthelot (*Ann. Chim. Phys.*, 1858, [iii], **52**, 97) stated that one-third of the residue obtained after the removal of hydrogen chloride from the products of interaction of equal volumes of methane and chlorine in diffused daylight was methyl chloride. J. Walter (D.R.-P. 222919) has patented a method of chlorinating methane under the action of light, whilst C. W. Bedford (*J. Ind. Eng. Chem.*, 1916, **10**, 1090) effects the chlorination of natural gas in a chamber containing ice with light from the white flame arc. The latter investigator states that the principal liquid products of the reaction are methylene dichloride and chloroform, up to 40 per

cent. of methyl chloride being present in the gases removed from the chamber after the reaction has been proceeding for a few minutes.

The present work was originally undertaken in order to determine whether it was possible to convert a sufficiently large proportion of the chlorine into methyl chloride to employ the reaction as an economic method of synthesising methyl alcohol on the large scale, as it has been shown by D. L. Chapman that methyl chloride can be almost quantitatively hydrolysed to methyl alcohol under the proper conditions. It was found, however, that not more than 25 per cent. of the chlorine forms methyl chloride in a mixture of $2\frac{3}{4}$ volumes of methane to 1 volume of chlorine, and only 10—13 per cent. in a mixture of equal volumes.

EXPERIMENTAL.

In the first series of experiments, natural gas from a blower in South Wales, containing a high percentage of methane, and commercial liquid chlorine were used, no attempt being made to purify them, except that they were dried, the marsh gas by passage through a long tube of calcium chloride, the chlorine by concentrated sulphuric acid. Preliminary experiments made with mixtures of marsh gas and chlorine in the ratio 2 : 1 showed that there was no combination in the dark, a slow combination under the influence of light from an ordinary 60-watt metallic filament lamp placed 30 cm. from the reaction vessel, and a much more rapid combination if an arc light was used. It was incidentally observed that if the gases contained a very small amount of nitrosyl chloride, practically no action took place, even in the strongest light.

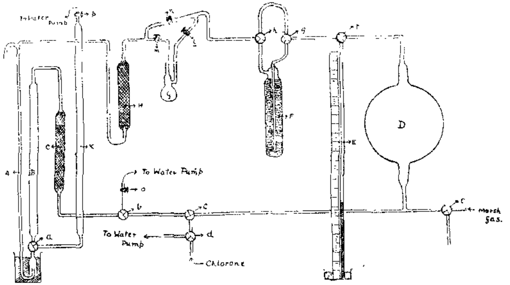
The quantitative estimation of the methyl chloride produced in the photochemical interaction of measured volumes of chlorine and marsh gas was effected with the aid of the apparatus depicted on p. 185.

Method of Separation of the Products of the Reaction.—The hydrogen chloride formed was easily removed by circulation through the tubes of soda-lime. The separation of the methyl chloride from the higher chlorinated products was more difficult, but advantage was taken of the large difference between the boiling points of methyl chloride and these other products, the various boiling points being:

Methyl chloride	−24·1°
Methylene dichloride	41·6°
Chloroform	61·2°
Carbon tetrachloride	76·7°

The method adopted, therefore, was to condense the methylene dichloride, chloroform, and carbon tetrachloride in the small condensing apparatus by a freezing mixture of carbon dioxide and ether and then to raise the temperature of the condensing apparatus to 0°, when any condensed methyl chloride evaporates, and this, *together with the uncondensed methyl chloride, is then condensed* in the charcoal tube, the latter being kept at 0°. A small amount of marsh gas also condenses in the charcoal, but by a test experiment made with a mixture of marsh gas and methyl chloride (prepared by the method due to Groves, *Journ. Chem. Soc.*, 1874, **27**, 641), it was shown that, provided the charcoal was kept at 0°, the

FIG 1.



A—Sprengel pump.

B—Tube in which the gases pumped out by the pump could be collected.

C—Tube packed with soda-lime to absorb hydrogen chloride formed in the reaction.

D—The reaction vessel of about 1750 c.c. capacity.

E—Manometer.

F—Tube packed with wood charcoal.

G—A small condensing apparatus capable of being inserted in a thermos flask.

H—Tube packed with calcium chloride and soda-lime.

K—Tube communicating through a three-way tap with the collector *B*.

The three-way taps in the apparatus are denoted by *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h*; and the two-way taps by *l*, *m*, *n*, *o*, and *p*.

The various portions of the apparatus were divided into four volumes:

V— From two-way tap *o* through *b*, *c*, *D* to *f*.

V_1—From three-way tap *b* through *C* to a fixed mark on the collector *B*.

V_2—From three-way tap *f* through *g*, *h* (omitting the charcoal tube *F*) to two-way taps *l* and *n* on the condensing apparatus *G*.

V_3—The volume of the condensing apparatus between taps *l* and *m*.

condensed marsh gas could be pumped off without removing any appreciable amount of the methyl chloride. The latter could be pumped off if the charcoal tube was heated to 300° by immersion in a tube of concentrated sulphuric acid. No attempt was made to separate the higher chlorinated products of the reaction from each other.

Experimental Details.—The method of conducting an experiment was as follows:

(1) The entire apparatus was first exhausted by the Sprengel pump.

(2) Marsh gas, dried by passing slowly through a tube packed with calcium chloride, was then admitted to the volume, V, through tap *e* until the required amount as shown by the manometer had been admitted.

(3) The three-way tap *b* was then opened to allow the marsh gas to fill the volume, V_1 also.

(4) Chlorine, dried by concentrated sulphuric acid, was then admitted through tap *c* into the volume, V, until the required amount had beeu admitted.

Note.—The admission of chlorine was always carried out in red light.

(5) The chlorine was then swept out of the capillary tuhes into the reaction globe, D, by increasing the pressure ou the marsh gas in the volume, V_1, hy means of mercury admitted into the collector from the side-tube K, and then momentarily opening tap *b*.

(6) The mixture was allowed to remain overnight to ensure that the chlorine had completely diffused through the marsh gas. From daybreak (ahout 5 a.m.) until 9 a.m. the mixture was exposed to daylight admitted through the windows of the laboratory, and then, although the green colour of the chlorine had completely disappeared, it was exposed for about one hour to the arc light to make sure that combination was complete. That this was so was further shown by the fact that the mercury in the apparatus was not attacked during the remainder of the experiment.

(7) The condensing apparatus was then immersed in a freezing mixture of carbon dioxide and ether, and the gaseous mixture circulated through the whole of the apparatus (except the charcoal tube) hy means of the Sprengel pump. When the manometer indicated that no further condensation would occur, circulation was stopped.

(8) Iced water was then substituted for the carhon dioxide and ether, the charcoal tube also surrounded hy iced water, tap *m* closed, tap *n* opened, and circulation recommenced, this time through the charcoal tube.

(9) When condensation was complete, tap *l* was closed, and the apparatus from tap *f* on the manometer to the fall tube of the Sprengel pump (including the charcoal tube) exhausted. When this was complete, the difference between the combined pressures of the chlorine and marsh gas originally admitted and the pressure of the residual marsh gas gave the pressure due to the now condensed products of the reaction.

(10) The charcoal tube was then immersed in a tube of concentrated sulphuric acid, which was heated to 300°, and the methyl chloride evolved was pumped into the volumes, $V + V_1$, of the apparatus. It was found that the last traces of methyl chloride could be more easily removed if marsh gas was admitted three or four times to the charcoal tube from the reaction vessel, *C*. The increase in pressure observed when all the methyl chloride had passed off was therefore the pressure of the methyl chloride.

Note.—By removing the small condensing apparatus, it was possible to determine the weight of the higher chlorinated products of the reaction, namely, methylene dichloride, chloroform, and carbon tetrachloride.

Experiments.—Two experiments were made with marsh gas and chlorine in the proportions:

(*a*) Marsh gas to chlorine = 2·80 : 1·0.
(*b*) Marsh gas to chlorine = 1·075 : 1·0.

A third experiment was made with pure methane, which was prepared by the method described by Gladstone and Tribe (T., 1884, **45**, 154) from a mixture of methyl iodide and methyl alcohol dropped on to the zinc-copper couple. The methane evolved was passed through a thin-walled vessel surrounded by a freezing mixture of ice and calcium chloride to remove any methyl iodide, then through two tubes containing concentrated sulphuric acid to remove alcohol, and finally collected over water. In this experiment, the proportions were:

(*c*) Methane to chlorine = 1·12 : 1·0.

The results obtained in these experiments are given below:

Experiment.	Percentage of chlorine converted to methyl chloride.	Percentage of chlorinated marsh gas (methane in Expt. 3) converted to methyl chloride.
1	24·5	45·9
2	9·9	22·7
3	13·1	27·7

The results show that the proportion of chlorine converted to methyl chloride is too low to make the process an economical one for the preparation of methyl alcohol from methyl chloride prepared in this manner. No analysis was made of the easily con-

densed products of the reaction (methylene dichloride, chloroform, and carbon tetrachloride), but there is reason to believe that the amounts of these formed were substantially the same as those found by Bedford (*loc. cit.*) working with natural gas and chlorine in the proportion of 7:1. Bedford analysed the liquid product obtained, and found it to contain: methylene dichloride, 35; chloroform, 35; carbon tetrachloride, 5; chloroethanes, 20 per cent.; whilst the portion dissolved in the water contained: methylene dichloride, 61; chloroform, 28; carbon tetrachloride, 1·5; chloroethanes, 6 per cent.

The Conversion of Methyl Chloride to Methyl Alcohol and Methyl Acetate.

The following details have been very kindly supplied to me by Mr. D. L. Chapman:

It is well known that the hydrolysis of alkyl chlorides presents difficulties. E. Szarvasy (*J. Soc. Chem. Ind.*, 1916, **35**, 707) showed that methyl chloride can be slowly hydrolysed by heating it with alkali to 140° under a pressure of 20—24 atmospheres, and Lacy has shown that the time of hydrolysis is reduced by adding lime to the alkali. Hibbert and Brooks (*J. Amer. Chem. Soc.*, 1916, **38**, 1368) have also conducted an investigation on the preparation of amyl alcohol from amyl chloride under similar conditions. They have also investigated the preparation of the acetate by the action of amyl chloride on sodium acetate. The yields never exceeded 50 per cent., as the amyl alcohol and amyl acetate were both partly converted into amylene. Kaufler (Brit. Pat. 2779 and 3133 of 1913), using a porous and voluminous form of sodium acetate, converted the alkyl chlorides into acetates at a lower temperature than with the ordinary fused sodium acetate, and he recommends the addition of a small quantity of copper acetate to the sodium acetate, but Hibbert and Brooks found cuprous acetate ineffective as a catalyst.

EXPERIMENTAL.

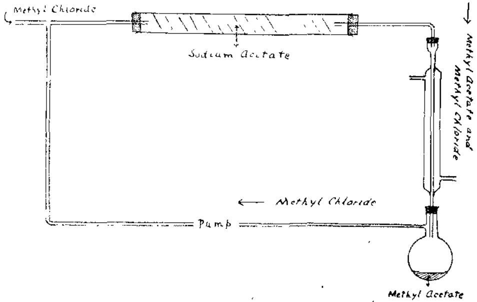
The methyl chloride was prepared by the method due to Groves. It was washed with sodium carbonate solution, scrubbed with concentrated sulphuric acid to remove methyl ether and the vapour of methyl alcohol, and then passed through the reaction tube heated in a gas furnace, which was maintained at a constant temperature by means of a thermoregulator.

Preparation of Methyl Acetate.—Using fused sodium acetate, methyl chloride begins to act at about 280°, and above 300° the

action is moderately rapid at the start, but soon falls off quickly, owing, no doubt, to the formation of a protective layer of sodium chloride on the surface of the sodium acetate. Moreover, if the reaction is continued, the liquid product contains only 89 per cent. of methyl acetate, 2·8 per cent. of the impurity being acetone, the remainder of the impurity not being identified. The residue left in the tube was found to be charred, but still contained some sodium acetate.

When sodium benzoate in the form of a very voluminous and porous network of crystals (prepared by adding the theoretical amount of sodium carbonate to a solution of benzoic acid, and then evaporating the solution of sodium benzoate) was used instead of

FIG. 2.



sodium acetate, it was found that the methyl chloride was converted quantitatively to methyl benzoate at 300—305°, the residue left in the tube being quite colourless. This was undoubtedly due to the porous condition of the sodium benzoate, and consequently suggested that the reaction, using sodium acetate, would also be complete if the sodium acetate were in a similar porous condition. A porous form of sodium acetate can be obtained by the action of glacial acetic acid on sodium carbonate, but to convert the whole of the carbonate into acetate, an excess of acetic acid must be used, and this is difficult to remove completely. It was found that a much more convenient method consisted in simply drying hydrated sodium acetate at 140°. Using the sodium acetate in this form, the methyl chloride was almost completely converted into methyl acetate. The apparatus used is depicted above.

The reaction tube was kept at 290° for four hours, and at 295—297° for a further four hours. At the end of this time, methyl acetate was still slowly distilling over. It was found to be essential to stop the reaction when about 60—70 per cent. of the sodium acetate had been decomposed, and the unchanged acetate can be easily recovered from the residue by crystallisation or obtained as acetic acid by treating the residue with the calculated amount of hydrochloric acid and then distilling.

Preparation of Methyl Alcohol.—Preliminary experiments showed that below 270° methyl chloride and steam do not interact at all, whilst between 270° and 320° only small quantities of methyl alcohol and hydrogen chloride were produced. Consequently, attempts to hydrolyse methyl chloride by steam were discontinued. It was found, however, that methyl chloride acts on slaked lime and soda-lime at a convenient rate to give methyl alcohol, but with soda-lime some of the alcohol is lost, owing to the action of the alkali on it to give hydrogen and sodium formate. It was then found that, nsing the same apparatus as was used for the preparation of methyl acetate, but with slaked lime kept at 300° in place of the sodium acetate, the conversion of methyl chloride into methyl alcohol was also almost quantitative, a small loss being due to the formation of some methyl ether from the alcohol by loss of water.

Conclusions.

(1) The photochemical interaction between methane and chlorine never stops at the first possible stage to give only methyl chloride, but always continues further, giving a mixture of all the possible chlorinated products, in which methylene dichloride and chloroform predominate.

(2) Methyl chloride can be completely converted to methyl acetate by passing it over porous sodium acetate at 290—297°.

(3) Methyl chloride can be almost completely converted to methyl alcohol by passing it over slaked lime at 300°.

My best thanks are due to Mr. D. L. Chapman for his advice and help during the progress of the work, and also to the Department of Scientific and Industrial Research for a grant enabling the work to be carried out.

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XXIV.—*Studies in the Resolution of Racemic Acids by Optically Active Alcohols. Part I. The Resolution of* r-*Tartaric Acid by* l-*Borneol.*

By HENRY WREN, HOWELL WILLIAMS, and WILLIAM WHALLEY MYDDLETON.

THE possibility of using optically active alcohols for the resolution of racemic acids and, conversely, of active acids for the fission of racemic alcohols appears to have been first suggested by Frankland (Pasteur Memorial Lecture, T., 1897, **71**, 696), but efforts in this direction have generally met with little success. Thus, Frankland and Price (T., 1897, **71**, 253) found that resolution was not effected by crystallisation of *d*-amyl *r*-dibenzoylglycerate, whilst McKenzie (T., 1904, **85**, 384) was unable to resolve *l*-menthyl *r*-mandelate by repeated crystallisation. The latter substance has been the subject of extended investigation by Findlay and Miss Hickmans (T., 1907, **91**, 905), who found, by observation of the freezing-point curves, that *l*-menthyl *r*-mandelate exists in the liquid state at the temperature of its melting point, at which it is dissociated into its components to the extent of about 50 per cent., whilst, subsequently (T., 1909, **95**, 1386), they showed by measurement of its solubility that it cannot be resolved by crystallisation from aqueous or absolute alcohol at any temperature above -15°. Similarly, McKenzie and Wren (T., 1907, **91**, 1222) observed that di-*l*-bornyl *r*-tartrate was not resolved into its diastereoisomerides by repeated crystallisation from methyl alcohol.

The only completely successful instance of a resolution of this type which appears to have been recorded up to the present is that described by Rupe and Häussler (*Annalen*, 1909, **369**, 324), who found that *l*-menthyl *l*-β-phenylbutyrate crystallises from the product of the action of *l*-menthol on *r*-β-phenylbutyryl chloride, and that it can be converted into *l*-β-phenylbutyric acid by treatment with alcoholic potassium hydroxide solution. Subsequently, Rupe and Kerkovius (*Ber.*, 1912, **45**, 1398) showed that *l*-menthyl *dl*-αβ-diphenylpropionate can be separated into its diastereoisomerides by fractional crystallisation from alcohol, but they were unable to isolate the corresponding acids in a condition even approximating to optical purity on account of the great readiness with which racemisation occurred when the esters were hydrolysed with alcoholic alkali.

The esters which have been investigated in this manner are all

normal in type. A short time ago Wren and Still (T., 1917, **111**, 513), during the course of an examination of the *l*-menthyl esters of the diphenylsuccinic acids, observed that, whilst *l*-menthyl hydrogen *r*-diphenylsuccinate is not resolved by crystallisation from light petroleum, its sodium salt could be partly resolved by crystallisation from water or by agitating its aqueous suspension with ether, whilst fission also occurred when the potassium salt was fractionally extracted with boiling ether. It therefore appeared possible that the salts of acid esters of racemic acids and optically active alcohols might lend themselves to purposes of resolution, and a series of experiments has been made in this direction. As acid, tartaric acid was selected both on account of its inherent stereochemical interest and ready availability. The choice of alcohol is much more restricted, since there are but few of these substances which can be obtained readily in suitable quantity and in a condition of optical purity; *l*-borneol and *l*-menthol naturally suggested themselves, and preference was accorded to the former, since it was considered that it would be more likely to yield well-crystallised esters, the behaviour of which could be studied in a variety of solvents.

The bulk of the requisite *l*-bornyl hydrogen *dl*-tartrate was prepared by mixing equal weights of the corresponding diastereoisomerides, which are conveniently prepared by the semi-hydrolysis of the appropriate normal esters, and are beautifully crystalline substances; under the conditions described in the experimental section, racemisation by alkali does not occur to any appreciable extent, since the acid esters obtained by hydrolysis are identical in all respects with those isolated as by-products in the esterification of the active acids with *l*-borneol.

The results of the investigation are somewhat unexpected, since it is found that *l*-bornyl hydrogen *dl*-tartrate is itself resolvable by crystallisation from every solvent which has been examined. The process has been carried to completion from chloroform, and potassium hydrogen *d*- and *l*-tartrates have been isolated in the pure state, whilst fission has also been shown to occur when water, benzene, toluene, or carbon tetrachloride is employed; in every case, *l*-bornyl hydrogen *d*-tartrate separates first. The sodium and barium salts, on the other hand, do not appear to be well adapted for resolution, although distinct evidence of the separation of the diastereoisomerides from aqueous solution has been obtained in each case. It is noticeable that the salts of *l*-bornyl hydrogen *l*-tartrate appear to be the more sparingly soluble, but the differences in solubility are less marked than in the case of the acid esters themselves.

Experimental.

*Preparation of Di-*l*-bornyl* d*-Tartrate and of* l*-Bornyl Hydrogen* d*-Tartrate.*

An intimate mixture of finely-powdered *d*-tartaric acid (70 grams) and *l*-borneol (200 grams) was heated in an intermittent current of dry hydrogen chloride during sixteen hours at 120°; the product was dissolved in ether, and the ethereal solution washed with aqueous sodium carbonate (solution A). After removal of the solvent, the residue was distilled with steam to remove excess of *l*-borneol, and the crude ester was purified by crystallisation from rectified spirit until the specific rotation of successive crops remained constant. The yield of ester after one crystallisation was 140 grams.

*Di-*l*-bornyl* d*-tartrate* separates from slightly aqueous alcohol in small, colourless needles. It is freely soluble in cold ether, chloroform, acetone, toluene, carbon tetrachloride, or carbon disulphide, but less readily so in cold alcohol or light petroleum. It melts at 132·5—133·5°:

0·1598 gave 0·3993 CO_2 and 0·1318 H_2O. C=68·1; H=9·2.

$C_{24}H_{38}O_6$ requires C=68·2; H=9·1 per cent.

The following observations of the specific rotation were made:

In chloroform solution:

$$l=2,\ c=2\cdot0275,\ \alpha_D^{13\cdot5}\ -0\cdot21^\circ,\ [\alpha]_D^{13\cdot5}\ -5\cdot17^\circ.$$

In acetone solution:

$$l=2,\ c=2\cdot275,\ \alpha_D^{14}\ -0\cdot26^\circ,\ [\alpha]_D^{14}\ -5\cdot71^\circ.$$

In benzene solution:

$$l=2,\ c=2\cdot1605,\ \alpha_D^{12}\ +0\cdot15^\circ,\ [\alpha]_D^{12}\ +3\cdot46^\circ.$$

The aqueous-alkaline solution A (see above) was acidified and extracted with ether, whereby a small quantity of *l*-bornyl hydrogen *d*-tartrate was isolated, which, after being crystallised from toluene, melted at 158° and had $[\alpha]_D^{12}$ −6·05° in ethyl-alcoholic solution; it was thus identical with the main bulk of the acid ester, which was prepared in the following manner. Di-*l*-bornyl *d*-tartrate (130 grams) was dissolved in a hot mixture of alcohol (250 c.c.) and water (130 c.c.), and a hot solution of the theoretical quantity of aqueous-alcoholic potassium hydroxide (1·856*N*, 167 c.c.) was rapidly added; the temperature of the mixture rose spontaneously to the boiling point, at which it was maintained for a few minutes, when hydrolysis was complete. The neutral solution was evaporated to remove alcohol, water was added, and the liberated borneol was separated by means of ether. The aqueous solution was acidified with hydrochloric acid and extracted with ether, whereby 55 grams of nearly

pure acid ester were isolated; the substance was crystallised from chloroform until successive crystallisations caused no change in the specific rotation of the product.

l-*Bornyl hydrogen* d-*tartrate* separates from boiling chloroform or toluene in shining leaflets. It is freely soluble in cold ethyl alcohol, acetone, or ether, moderately so in hot water, toluene, or chloroform, and very sparingly so in carbon disulphide, carbon tetrachloride, or light petroleum. It melts at 158—158·5°:

0·1600 gave 0·3451 CO_2 and 0·1122 H_2O. C=58·8; H=7·8.

$C_{14}H_{22}O_6$ requires C=58·7; H=7·8 per cent.

The specific rotation was observed in ethyl alcohol and in acetone.

In ethyl-alcoholic solution:

$l=2$, $c=2·1805$, $\alpha_D^{14·5}$ −0·19°, $[\alpha]_D^{14·5}$ −5·7°.

$l=2$, $c=7·575$, α_D^{15} −0·99°, $[\alpha]_D^{15}$ −6·5°.

In acetone solution:

$l=2$, $c=2·3795$, α_D^{14} −0·06°, $[\alpha]_D^{14}$ −1·26°.

Aqueous solutions of *l*-bornyl hydrogen *d*-tartrate are somewhat surprisingly sensitive to the presence of slight local excesses of alkali hydroxides; the alkali salts are therefore most conveniently prepared by gently warming aqueous solutions of calculated amounts of the acid ester and of the requisite alkali hydrogen carbonate.

Potassium l-*bornyl* d-*tartrate* separates from water, in which it is rather freely soluble, in aggregates of silky needles:

0·9980 * lost 0·1055 at 105°. H_2O=10·56.

$C_{14}H_{21}O_6K,2H_2O$ requires H_2O=10·0 per cent.

0·2408 † gave 0·0630 K_2SO_4. K=11·74.

$C_{14}H_{21}O_6K$ requires K=12·05 per cent.

Sodium l-*bornyl* d-*tartrate* is less readily soluble in water than the corresponding potassium salt:

1·0024 * lost 0·0960 at 105°. H_2O=9·57.

$C_{14}H_{21}O_6Na,2H_2O$ requires H_2O=9·56 per cent.

0·4873 † gave 0·1100 Na_2SO_4. Na=7·3.

$C_{14}H_{21}O_6Na$ requires Na=7·5 per cent.

*Preparation of Di-*l-*bornyl* l-*Tartrate and of* l-*Bornyl Hydrogen* l-*Tartrate.*

The requisite *l*-tartaric acid was prepared by the resolution of *r*-tartaric acid by cinchonine in aqueous solution in accordance with the directions of Marckwald (*Ber.*, 1896, **29**, 42); for the present purposes, the isolation of the free acid was unnecessary, and it was

* Air-dried. † Dried at 105—110°.

found more advantageous to separate the sparingly soluble potassium hydrogen salt. This was converted into di-*l*-bornyl *l*-tartrate by *l*-borneol in the presence of hydrogen chloride in the same manner as has been described for the corresponding *d*-ester. The crude normal ester was purified by crystallisation from alcohol and finally from light petroleum.

Di-l-*bornyl* l-*tartrate* separates from light petroleum in large, ill-defined, hexagonal plates; it is freely soluble in the boiling, sparingly so in the cold, solvent. It dissolves readily in cold chloroform, benzene, toluene, or acetone, and moderately readily in cold ethyl alcohol. It is more readily soluble than its diastereoisomeride in all the solvents investigated. It melts at 118—118·5°:

0·1544 gave 0·3860 CO_2 and 0·1272 H_2O. C=68·2; H=9·2.

$C_{24}H_{36}O_6$ requires C=68·2; H=9·1 per cent.

The specific rotation was observed in the following solvents:

In chloroform solution:

$l=2,\ c=2·520,\ \alpha_D^{15}\ -3·60°,\ [\alpha]_D^{15}\ -71·4°.$

In benzene solution:

$l=2,\ c=2·416,\ \alpha_D^{14·5}\ -3·75°,\ [\alpha]_D^{14·5}\ -77·6°.$

In acetone solution:

$l=2,\ c=2·5405,\ \alpha_D^{11·5}\ -2·90°,\ [\alpha]_D^{11·5}\ -71·3°.$

The mean of the specific rotations of di-*l*-bornyl *d*-tartrate (−5·17°) and di-*l*-bornyl *l*-tartrate (−71·4°) when dissolved in chloroform is −38·3°, a value which is in good agreement with the figure (−38·5°) found by McKenzie and Wren (T., 1907, **91**, 1221) by direct observation with di-*l*-bornyl *r*-tartrate.

l-Bornyl hydrogen *l*-tartrate was isolated in small amount as a by-product of the preparation of the normal ester; it melted at 130·5—131° and had $[\alpha]_D^{1}$ −52·2° (c=2·6608) in ethyl-alcoholic solution. It was identical in all respects with the bulk of the hydrogen ester, which was prepared by the semi-hydrolysis of the normal ester in a manner similar to that described for the diastereoisomeride.

l-*Bornyl hydrogen* l-*tartrate* separates from benzene in shining leaflets; it dissolves readily in the boiling, sparingly in the cold, solvent. It is freely soluble in cold chloroform, alcohol, acetone, or hot water, moderately so in boiling carbon disulphide or carbon tetrachloride, and sparingly so in boiling light petroleum (b. p. 60—80°). In general, it is very noticeably more readily soluble in all solvents than is its diastereoisomeride. It melts at 130·5—131°:

0·1637 gave 0·3519 CO_2 and 0·1116 H_2O. C=58·6; H=7·6.

$C_{14}H_{22}O_6$ requires C=58·7; H=7·8 per cent.

The specific rotation was determined in ethyl-alcoholic solution:

$$l=2,\ c=2\cdot985,\ \alpha_D^{13}\ -2\cdot47°,\ [\alpha]_D^{13}\ -51\cdot7°.$$

l-*Bornyl hydrogen* dl-*tartrate* was prepared by dissolving equal weights of the diastereoisomerides in acetone and rapidly removing the solvent:

0·1543 gave 0·3316 CO_2 and 0·1057 H_2O. C = 58·6; H = 7·7.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·8 per cent.

The *specific rotation was observed in ethyl-alcoholic solution:*

$$l=2,\ c=2\cdot7792,\ \alpha_D^{14\cdot2}\ -1\cdot57°,\ [\alpha]_D^{14\cdot2}\ -28\cdot2°.$$

The mean of the values observed for *l*-bornyl hydrogen *d*-tartrate and *l*-bornyl hydrogen *l*-tartrate under closely similar conditions is −28·7°.

Resolution of l-*Bornyl Hydrogen* dl-*Tartrate by Crystallisation from Chloroform.*

Equal weights of *l*-bornyl hydrogen *d*-tartrate and *l*-bornyl hydrogen *l*-tartrate (20 grams of each) were mixed and dissolved in boiling chloroform (150 c.c.); on cooling the solution, crystallisation occurred after some time. The mixture was allowed to remain at the ordinary temperature for about eight hours, after which it was filtered. The crystalline crop weighed 9·6 grams and had $[\alpha]_D$ −9·8° in ethyl-alcoholic solution. It was again crystallised from the same solvent (90 c.c.), whereby 5 grams of material were obtained which melted at 157—158·5° and had $[\alpha]_D^{10\cdot8}$ −7·2° in alcoholic solution. A further crystallisation yielded pure *l*-bornyl hydrogen *d*-tartrate, which was identified by analysis (Found, C = 58·8; H = 7·7. Calc., C = 58·7; H = 7·8 per cent.), by melting point, 157·5—158°, both alone and when mixed with an approximately equal amount of synthetic *l*-bornyl hydrogen *d*-tartrate and by determination of the specific rotation in ethyl-alcoholic solution:

$$l=2,\ c=2\cdot392,\ \alpha_D^{11\cdot8}-0\cdot32°,\ [\alpha]_D^{11\cdot8}-6\cdot6°.$$

Elimination of the *l*-bornyl group was readily effected by the action of a slight excess of aqueous potassium hydroxide solution (0·931*N*) on the aqueous suspension of the ester. On addition of alkali, the odour of borneol became immediately very apparent. After remaining for about two hours at the ordinary temperature the mixture was gradually heated on the water-bath. The precipitated borneol was removed by filtration, and the filtrate was extracted with ether to complete the elimination of the borneol. The aqueous solution was then treated with standard hydrochloric acid in the quantity necessary for the formation of potassium

hydrogen tartrate, when the latter salt immediately separated; it was purified by crystallisation from water and dried in a vacuum over calcium chloride (0·2038 neutralised 10·95 c.c. $N/10$-potassium hydroxide solution. Calc., 10·83 c.c. 0·1681 gave 0·0775 K_2SO_4. K = 20·7. Calc., K = 20·8 per cent.).

As the sparing solubility of potassium hydrogen tartrate in water does not render it a suitable substance for polarimetric analysis it was dissolved in the quantity of aqueous N-potassium hydroxide necessary to form the normal salt and the solution was diluted to the mark with water.

3·113 Grams of potassium hydrogen tartrate, dissolved in potassium hydroxide and the solution made up to 25 c.c. with water, had α_D^{15} + 8·48° in a 2-dcm. tube, when $[\alpha]_D^{15}$ + 28·3°. (The concentration of the solution expressed in terms of the normal tartrate is 14·972 grams per 100 c.c.). This value agrees well with the data recorded in the literature for normal potassium *d*-tartrate; thus, Schütt (*Ber.*, 1888, **21**, 2586) gives $[\alpha]_D^{20}$ + 28·61° for c = 19·23 and $[\alpha]_D^{20}$ + 28·01° for c = 9·62, whilst Thomsen (*J. pr. Chem.*, 1886, [ii], **34**, 89) found $[\alpha]_D^{15}$ + 29·02° for c = 20·38 and + 28·34° for c = 9·62.

The filtrate obtained from the first crystallisation of the *l*-bornyl hydrogen *dl*-tartrate (see above) was allowed to evaporate spontaneously, whereby 29·3 grams of material were obtained which had $[\alpha]_D$ − 33·7° in ethyl-alcoholic solution. It was crystallised from boiling chloroform (50 c.c.), when the crop which separated (9 grams) had $[\alpha]_D$ − 12·17°, whilst the product obtained by evaporation of the filtrate weighed 20 grams and had $[\alpha]_D$ − 40·0° in alcohol. The latter was decomposed with aqueous potassium hydroxide solution and the potassium salts were converted into the mixture of *r*- and *l*-tartaric acids. The bulk of the former was removed by cautious crystallisation of the mixed acids from a small quantity of water. The acids contained in the filtrate were transformed into their potassium hydrogen salts, which were subsequently crystallised from water, ultimately yielding a small amount of potassium hydrogen *l*-tartrate in a state of purity (Found, K = 20·7. Calc., K = 20·8 per cent.).

0·6315 Gram dissolved in the requisite quantity of N-potassium hydroxide solution and diluted to 25 c.c. with water had α_D − 1·65° at 16° in a 2-dcm. tube, whence $[\alpha]_D^{16}$ − 27·2°. (The concentration of the solution expressed as normal tartrate is 3·036 grams per 100 c.c.). By extrapolation from Schütt's data (*loc. cit.*) the pure anhydrous potassium *l*-tartrate has $[\alpha]_D^{20}$ − 27·4° at this concentration.

Experiments on the Resolution of l-*Bornyl Hydrogen* dl-*Tartrate from Solvents other than Chloroform.*

From Carbon Tetrachloride.—Equal weights of the diastereoisomerides (0·8727 gram in each case) were mixed and dissolved in boiling carbon tetrachloride (520 c.c.). The solution was allowed to cool to the ordinary temperature; the crystals which separated had $[\alpha]_D$ −26·5°, whilst the material left on evaporation of the mother liquor had $[\alpha]_D$ −34·2° in ethyl-alcoholic solution.

From Water.—The mixed esters (1·7524 grams) were dissolved in hot water (30 c.c.); nothing separated from the cold solution, which was therefore seeded with a minute quantity of the *d*-ester, when a small crop slowly formed. The specific rotations of the crystals and of the portion which remained in solution were −6·9° and −31·1° respectively.

From Benzene.—1·9226 Grams of the mixed esters were dissolved in boiling benzene (40 c.c.); the cold solution deposited 1·6 grams of substance, which was further crystallised from 80 c.c. of the solvent. 1·05 Grams of material, having $[\alpha]_D$ −19·9° in alcohol, were obtained, whilst the residues left on evaporation of the successive filtrates had $[\alpha]_D$ −34·9° and −36·5° respectively.

From Toluene.—The solution of the mixed esters (1·8214 grams) in hot toluene (30 c.c.) deposited 1·57 grams of material, which was recrystallised from 100 c.c. of the solvent. The second crop had $[\alpha]_D$ −25·0° in ethyl-alcoholic solution, whilst the material obtained from the united mother liquors had $[\alpha]_D$ −35·5°.

Resolution of l-*Bornyl Hydrogen* dl-*Tartrate by Crystallisation of its Salts.*

Sodium Salt.—1·8472 Grams of the *dl*-ester were suspended in warm water (24 c.c.) and treated with sodium hydrogen carbonate in slight excess; a clear solution was readily obtained, from which crystals separated on cooling. The separated salt and that contained in the filtrate were converted into the hydrogen esters and polarimetrically examined in ethyl-alcoholic solution, when the values −29·4° and −28·0° respectively were observed for the specific rotations.

Barium Salt.—Equal weights of the diastereoisomerides (0·9571 gram in each case) were dissolved in water, and the solution was neutralised by the cautious addition of dilute aqueous barium hydroxide. The dense precipitate was dissolved in hot water (2 litres) and the solution was allowed to cool, when a crystalline crop gradually separated. The specific rotations of the hydrogen esters

obtained from the crop and filtrate were $-29{\cdot}3^\circ$ and $-26{\cdot}8^\circ$ respectively.

In the experiments which have just been described, the requisite *dl*-ester was obtained by mixing equal weights of the *d*- and *l*-esters. Preliminary experiments indicated, as was to be expected, that resolution can equally be effected starting from *r*-tartaric acid. Thus, in one case, the latter acid was completely esterified with *l*-borneol and the *l*-bornyl *r*-tartrate was treated with half the quantity of potassium hydroxide necessary for complete hydrolysis; the crude *l*-bornyl hydrogen *dl*-tartrate obtained in this way was repeatedly crystallised from benzene, when the specific rotations of the second, third, and fourth crops were $-27{\cdot}0^\circ$, $-23{\cdot}3^\circ$, and $-21{\cdot}1^\circ$ respectively. It is hoped to give a more complete account of this aspect of the case when the behaviour of the esters of racemic dibasic acids and optically active alcohols on subjection to partial hydrolysis has been more fully investigated.

The authors desire to express their thanks to the Research Fund Committee of the Royal Society for a grant which has defrayed part of the cost of the investigation.

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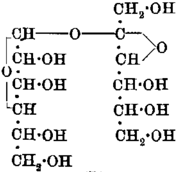
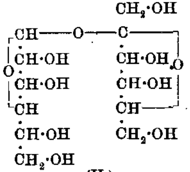
XXV.—*The Constitution of the Disaccharides. Part IV. The Structure of the Fructose Residue in Sucrose.*

By WALTER NORMAN HAWORTH.

A NEW constitutional formula for sucrose (I) was proposed in a former communication in this series, where it was shown that the



(I.)
(Glucose residue.) (Fructose residue.)
New sucrose formula.



(II.)
Fischer's formula for sucrose.

fructose residue contained in sucrose could not possess the structure generally assigned to it (Haworth and Law, T., 1916, **109**, 1314).

The data on which this conclusion was based may be summarised as follows: (1) On hydrolysis with dilute acids, octamethyl sucrose does not show the phenomenon of "inversion," as does sucrose whereas, in conformity with the usual experience, the cleavage of the methylated disaccharide ought to give rise to a molecular mixture of tetramethyl glucose and tetramethyl fructose which would be predominantly lævorotatory.

(2) This unexpected result was traceable to the fructose residue which, differing in structure from ordinary fructose, displayed a pronounced dextrorotation.

(3) The crystalline tetramethyl fructose (IV), isolated by Purdie and Paul (T., 1907, **91**, 296) during their study of the methylation of methyl fructoside, showed a specific rotation of $[\alpha]_D$ $-121°$ in aqueous solution, whilst the corresponding product derived from the hydrolysis of octamethyl sucrose by Haworth and Law (*loc. cit.*) was a liquid which distilled easily, but did not crystallise on nucleation with a specimen of Purdie and Paul's compound. Moreover, the new form of tetramethyl fructose was unstable towards permanganate and behaved uniformly as a sugar derivative of the γ- or supposed ethylene-oxide type.

Opportunity has again been taken to isolate this new form of tetramethyl fructose and to submit it to further constitutional study. The isolation of this compound in a state of purity from the products of hydrolysis of octamethyl sucrose was attended with much experimental difficulty. This was due to its occurrence along with the isomeric tetramethyl glucose, since the latter distils at approximately the same temperature as the methylated fructose fragment.

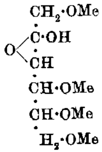
In the present series of experiments it has been found that the difficulty formerly experienced in separating the cleavage products vanishes if heptamethyl sucrose is substituted for the completely methylated biose in a parallel experiment. The advantage conferred by the use of heptamethyl sucrose is attributable to the nature of its scission products, which distil at temperatures sufficiently remote from each other to admit of easy separation by fractional distillation. The partly methylated biose was obtained by methylating sucrose in alkaline solution with methyl sulphate (Haworth, T., 1915, **107**, 12), and this has been shown to be a pure chemical individual, in which the fructose constituent is fully methylated, but only three methyl groups are present in the glucose component.

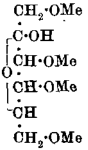
When heptamethyl sucrose was hydrolysed with 0·4 per cent. hydrochloric acid at 60° for six and a-half hours the specific rotation

diminished from $[\alpha]_D +64{\cdot}3°$ to $+52°$, and at the latter value remained constant. The products of this change consisted of a molecular mixture of a trimethyl and a tetramethyl hexose, which was easily separable by distillation at the Gaede pump. The first fraction distilled as a colourless, mobile liquid at 110—112°/0·35 mm., having n_D 1·4545, and gave analytical results corresponding with a tetramethyl hexose. A second fraction was collected as a viscid syrup, boiling at 170°/0·43 mm., showing n_D 1·4755, and analysis proved it to be a trimethyl hexose. The amounts of both fractions were approximately equal.

Clearly it was of importance to decide which of these individual fractions represented the glucose or fructose residue in the original sucrose. This point was established by submitting the trimethyl hexose to further methylation, when it was converted into a crystalline substance melting at 83°, showing $[\alpha]_D +84°$, and identical with tetramethyl glucose (compare Haworth and Law, *loc. cit.*, p. 1324), a result which afforded ample proof that the trimethyl hexose was a glucose derivative. Consequently, it follows that the tetramethyl hexose having the lower boiling point represented the fructose residue in sucrose.

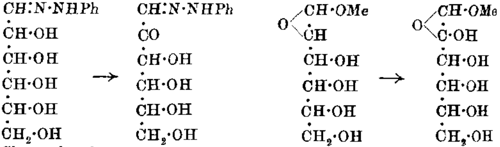
Attention has been focussed in the course of the present investigation on this specimen of tetramethyl fructose. In the previous communication on this subject (*loc. cit.*) an approximation only could be made as to the probable specific rotation of this compound in aqueous solution, and the value was tentatively given as $[\alpha]_D +29{\cdot}3°$. The correct value, determined experimentally for the first time, differs only slightly from this anticipated result, and is now recorded as $[\alpha]_D +31{\cdot}7°$. The snbstance is very unstable towards permanganate, and conforms to the new type of hexoses which have been provisionally named ethylene-oxide sugars. Further, the constitution previously assigned to the new variety of tetramethyl fructose (III) has been subjected to close experimental scrutiny:


(III).
Tetramethyl fructose (ethylene-oxidic).


(IV.)
Tetramethyl fructose (butylene-oxidic).

In allocating this structural formula (III) to the fructose residue

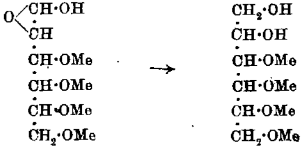
in sucrose the only basis on which one could proceed was the valuable group of facts recorded by Irvine, Fife, and Hogg during their investigation of the new variety of tetramethyl glucose (V), described as a γ-sugar (T., 1915, **107**, 524). These authors showed that a derivative of γ-glucose examined by them showed a remarkable capacity to increase its oxygen content to the extent of one atomic proportion during methylation with silver oxide and methyl iodide. Surprising though this behaviour may be, it finds a parallel in the oxidation of glucose with phenylhydrazine which gives rise to the glucosazone. It is established that in the latter case the oxidation change effects removal of the hydrogen atoms attached to the second carbon atom from the reducing end of the hexose chain. The analogy which has been drawn between the two reactions leads to the suggestion that in both cases oxidation is confined to the groups associated with the carbon atom which adjoins the reducing group:



Glucosephenylhydrazone (Fischer). Methyl glucoside (ethylene-oxidic). Hydroxymethyl glucoside.

The above formulæ are given in this simple form for the sake of clearness; it will be recognised that the two products of oxidation indicate only intermediate stages of the reactions which have been studied. The main point is, that if the analogy be admitted, the ethylene-oxide form of methyl glucoside is the only one that can hold for the new type of sugar derivative.

In order to furnish a proof of this structural arrangement, Irvine, Fife, and Hogg (*loc. cit.*) submitted a derivative of the new type of γ-sugar, namely, tetramethyl γ-glucose (V), to (*a*) reduction,

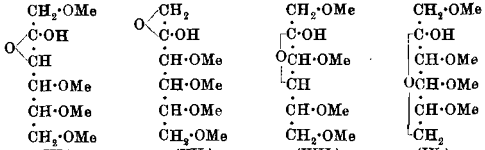


(V.) (VI.)

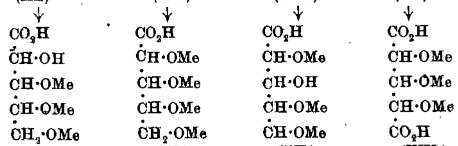
(*b*) oxidation. The product of reduction was a tetramethyl sorbitol (VI), which showed optical exaltation in the presence of boric acid, and thus, in the light of Böeseken's recent work (*Ber.*, 1913, **46**, 2612), the compouud coutained two hydroxyl groups attached to neighbouriug carbon atoms, a result which affords strong support to the ethylene-oxide formula of the sugar.

On the other hand, oxidation of the sugar (V) with permanganate gave rise to a unimolecular lactone, the formation of which would appear to be precluded if the ethylene-oxide structure were adopted as above. Whilst, therefore, this mode of representation was provisionally proposed for the new or γ-sugars, it was recognised that other interpretations were possible

Consequently, in the special case under review, namely, that of the fructose residue isolated from heptamethyl sucrose, it was considered of first importance to provide some additional experimental basis on which the structure assigned to this compound could rest. Apart from the butylene-oxide form of tetramethyl fructose (IV) which has been definitely characterised, there would appear to be no fewer than four possible formulæ by which the tetramethyl fructose isolated in the course of the present investigation may be represented; these are given as the following, and for the sake of comparison the oxidation products to which they may be expected to give rise are printed below in the vertical column:



(III.) (VII.) (VIII.) (IX.)



(X.) (XI.) (XII.) (XIII.)

	(X.)	(XI.)	(XII.)	(XIII.)
	$C_8H_{16}O_6$.	$C_9H_{18}O_6$.	$C_8H_{16}O_6$.	$C_8H_{14}O_7$.
C =	46·1	48·7	46·1	43·6
H =	7·7	8·1	7·7	6·4
OMe =	44·7	55·8	44·7	41·9

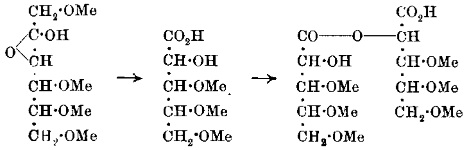
The choice of oxidising agent, namely, dilute nitric acid, was determined by the fact that oxidation of a sugar of the formula (IX), if effected with bromine water, would leave a primary alcohol group exposed, whilst nitric acid would oxidise both the reducing and primary alcohol groups. On submitting the specimen of tetramethyl fructose to oxidation with nitric acid at 60°, a viscid liquid was formed which distilled at 190—200°/1·8 mm., and analysis gave C=48·17; H=7·43; OMe=43·4. Such a result is not in agreement with any of the figures quoted above, although it approximates closely to those required for dehydration of two molecular proportions of $C_8H_{16}O_6$, namely, $C_{16}H_{30}O_{11}$, which requires C=48·24; H=7·54; OMe=46·7 per cent. A determination of molecular weight by the cryoscopic method gave 354; that required by the bimolecular anhydride is 398, whilst the unimolecular formulæ require approximately half this value.

Inspection of the formula (X) will indicate that this represents an α-hydroxy-acid, and may be referred to lactic acid as a type. It is well known that lactic acid undergoes conversion into an anhydride or semi-lactide, either by heating at 130—140°, or spontaneously at the ordinary temperature in a dry atmosphere. The formula (XII) admits of the possibility of the formation of a unimolecular β-lactone, since Nef has shown that mannono-β-lactone is easily formed, but passes into aqueous solution as regenerated mannonic acid (*Annalen*, 1914, **403**, 204). Nef also mentions the existence of bimolecular α-lactones, by which is meant substances analogous to the semi-lactide from lactic acid, which has already been quoted. On the other hand, formulæ (XI) and (XIII) do not admit of the possibility of dehydration except by the ordinary process of preparing acid anhydrides.

It was ascertained by analysis that, in the particular experiment under review, when the product derived from the oxidation of the tetramethyl fructose was isolated from aqueous solution by evaporation of the solvent, anhydride formation had already occurred, and a consideration of all the possible formulæ leads to the conclusion that this could only take place with an α-hydroxy-acid. It will be remembered that the oxidation product was found to possess the formula $C_{16}H_{30}O_{11}$, and is thus bimolecular. Moreover, the compound was acid towards litmus, and when titrated with alkali it behaved as an acid until about half the total alkali required for complete neutralisation had been added. From this point onward the substance exhibited all the properties of a lactone, absorption of additional alkali taking place with extreme slowness. The final result corresponded exactly with the requirements for a semi-

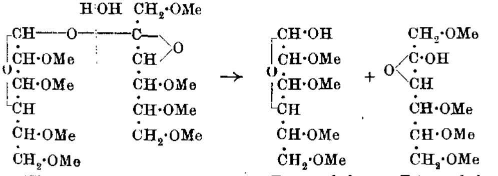
lactide (XIV) of the formula $C_{16}H_{30}O_{11}$, and full details will be found in the experimental part.

From these considerations it will be clear that the oxidation product must have been formed from an acid of formula (X), which in turn can *only* represent a product of degradation of a tetramethyl fructose having the formula (III):



(III.) (X.) (XIV.)

This result furnishes valuable evideuce in support of the constitutional formula (I) for sucrose, advanced in an earlier communicatiou by Haworth and Law (this series, Part I), and the hydrolysis of octamethyl sucrose therein described may now be formulated:



(Glucose residue.) (Fructose residue.) Octamethyl sucrose. → Tetramethyl glucose (butylene-oxidic.) + Tetramethyl fructose (ethylene-oxidic.)

A similar representation would apply to the hydrolytic cleavage of heptamethyl sucrose, except that in this case a butylene-oxide form of trimethyl glucose is obtained as the glucose constituent.

An explanation of the observed facts that, when free sucrose is hydrolysed, glucose and ordinary lævorotatory fructose are found as the products, is given in Part I. of this series. It is there stated that although the ethyleue-oxide form of fructose must first be produced, the hydrolysis is accompanied by a supplementary structural change involving the transformation of the fructose residue at the moment of cleavage into a butylene-oxide form. Such supple-

mentary changes are inhibited if the hydroxyl groups in sucrose are protected by methyl groups.

Although the additional evidence here contributed as to the structure of sucrose appears capable of no simple explanation other than that now offered, the constitution of the new form of tetramethyl fructose is being further investigated iu view of the importance of the issues.

EXPERIMENTAL.

Hydrolysis of Heptamethyl Sucrose.

Heptamethyl sucrose (28 grams), prepared by the method already described (Haworth, T., 1915, **107**, 12), was dissolved in 450 c.c. of 0·4 per cent. aqueous hydrochloric acid and the mixture heated in a water-bath maintained at 60°. Polarimetric readings were taken from time to time, and hydrolysis was complete in six and a-half hours:

Time.	l.	α_D.	$[\alpha]_D$.
5 minutes	2-dcm.	+8·0°	+64·3°
1 hour		7·0	
1½ hours		6·46	
3 ,, ...		6·76	
6½ ,, ...		6·74	+54·0

At this stage the acid was neutralised with barium carbonate, and the solution filtered and evaporated under diminished pressure in presence of a trace of barium carbonate. A syrupy residue remained, which was contaminated with barium salts. The product was dissolved in absolute alcohol, filtered to remove mineral matter and the solvent distilled. A further treatment with ether served to remove the whole of the suspended salts. Thereafter the residue was submitted to fractional distillation at the Gaede pump.

Nearly half the total product distilled as a colourless, mobile liquid at 110—120°/0·35 mm., whilst the remainder was collected at 154—170°/0·6 mm. On repeated refractionation of each portion two main fractions were obtained:

1. . . . b. p. 110—112°/0·32 mm. n_D 1·4545.
2. . . . b. p. 168—170°/0·43 mm. n_D 1·4755.

The latter substance was a viscid syrup, which failed to give an osazone on treatment with phenylhydrazine. On analysis it was shown to be a trimethyl hexose:

0·1206 gave 0·2149 CO_2 and 0·0888 H_2O. C=48·60; H=8·19.

0·1284 gave, by Zeisel's method, 0·3988 AgI. OMe=41·0.

$C_6H_9O_3(OMe)_3$ requires C=48·65; H=8·11; OMe=41·9 per cent.

This trimethyl hexose was submitted to further methylation by

methyl iodide and silver oxide. The product was thereafter hydrolysed with 8 per cent. hydrochloric acid at 100° for three hours in order to remove the glucosidic group and obtain the tetramethyl hexose. The latter was isolated in the usual way, and was found to consist of a liquid which quickly crystallised. Recrystallisation of the solid from light petroleum yielded characteristic prismatic needles, which were easily identified as tetramethyl glucose, melting at 83°, and showing no depression in melting point when mixed with a specimen of this sugar isolated on a previous occasion (T., 1916, **109**, 1324). The specific rotation was $[\alpha]_D$ +84° in equilibrium in water.

Since tetramethyl glucose of the butylene-oxide form was isolated as the result of this experiment, there could be no doubt that the trimethyl hexose distilling at the higher temperature in fraction (2) was a trimethyl glucose of the normal type. This showed $[\alpha]_D$ +55·7° in methyl alcohol and +56·0° in aqueous solution, and its further study will form the subject of a future communication.

A New Form of Tetramethyl Fructose (III).

The first fraction distilling at 110—112°/0·32 mm. was also found to boil at 154°/13 mm. It decolorised permanganate readily, and behaved generally as a γ-sugar. The following analytical results were obtained:

0·2220 gave 0·4141 CO_2 and 0·1700 H_2O. C=50·87; H=8·51.
0·1420 „ 0·5430 AgI. OMe=50·3.
$C_6H_8O_2(OMe)_4$ requires C=50·85; H=8·47; OMe=52·5 per cent.

The specific rotation of the sugar was determined.

Solvent.	$[\alpha]_D$.
Water..................	+31·7° (final reading)
Methyl alcohol	+21·3°

When the aqueous solution was catalysed with a trace of hydrochloric acid, the specific rotation increased to +32·6°.

Oxidation with Nitric Acid.—The tetramethyl fructose (4·75 grams) was oxidised by heating with dilute nitric acid (D 1·2) at 60° for five hours. The water and most of the nitric acid were removed by vacuum distillation at low temperature, and the residue was treated successively with absolute alcohol and ether, followed by distillation of the solvent and continued heating in the vacuum of the Gaede pump until the whole of the nitric acid was removed.

In a preliminary attempt to purify the residual syrup it was dissolved in ether and shaken in a separating funnel with small quantities of water. There remained in the ethereal layer about one-fifth of the original amount of the syrup, and after drying and

removal of solvent this small residue was dried in a stream of air in a vacuum, when it gave the following analytical results:

0·1550 gave 0·2754 CO_2 and 0·1076 H_2O. C=48·45; H=7·71.

$C_{16}H_{30}O_{11}$ requires C=48·24; H=7·54 per cent.

The portion remaining in the aqueous layer was now extracted with much ether and the solvent removed by distillation. The residue was dried by heating at 100° in the vacuum of the Gaede pump, and at this stage a sample was removed for analysis:

0·1803 gave 0·3154 CO_2 and 0·1233 H_2O. C=47·71; H=7·59.

The syrup was then distilled, when it was observed that very little decomposition occurred. A small first fraction was collected as an amber-coloured syrup distilling at 185—190°/1·8 mm., and a large second fraction was obtained, boiling at 190—200°/1·8 mm. and having $n_D=1·4575$. The first fraction was analysed as follows.

0·1236 gave 0·2210 CO_2 and 0·0829 H_2O. C=48·76; H=7·45.

The second fraction gave the figures:

0·1042 gave 0·1841 CO_2 and 0·0697 H_2O. C=48·17; H=7·43.

0·1092 ,, 0·3590 AgI. OMe=43·4.

$C_{10}H_{12}O_5(OMe)_6$ requires C=48·24; H=7·54; OMe=46·7 per cent.

This corresponds with an anhydro-acid (XIV) or semi-lactide $C_{16}H_{30}O_{11}$. The substance appeared to be hygroscopic, and quickly absorbed water from a moist atmosphere.

During the titration with *N*/10-sodium hydroxide the syrupy oxidation product behaved at first as an acid, and finally as a lactone. Phenolphthalein was used as indicator. 0·1192 Gram was dissolved in water and titrated with *N*/10-sodium hydroxide. The alkali was rapidly absorbed until 2·9 c.c. had been added; thereafter additional alkali was absorbed with extreme slowness at the ordinary temperature. On adding in all 10 c.c. and heating under reflux for a quarter of an hour, the cooled solution was neutralised with *N*/10-sulphuric acid and required 3·85 c.c. The total alkali which had combined with the compound was therefore 6·15 c.c. The theoretical amount required for an anhydro-acid $C_{16}H_{30}O_{11}$, is 5·98 c.c.

A determination of molecular weight in benzene solution was carried out by the cryoscopic method, when the values found were 354·1 and 343·5. The anhydro-acid, $C_{16}H_{30}O_{11}$, requires M.W.=398.

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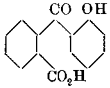
[*Received, February 2nd*, 1920.]

XXVI.—*Phthaleins and Fluorans.*

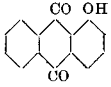
By MAURICE COPISAROW.

THE object of this investigation was the study of the constitution and conditions of formation of some members of the phthalein and fluoran series. Whilst certain phenols, such as resorcinol and pyrogallol, react with phthalic anhydride in the absence of any dehydrating agent, in most other cases some such agent is required for the condensation to take place. These condensing agents, in conjunction with the experimental conditions, influence not only the yield, but also the character of the products. In most cases, the formation of phthaleins (III) is accompanied by the production of substances belonging to the *o*-ketonic acid (I) (Deichler and Weizmann, *Ber.*, 1903, **36**, 547; Copisarow and Weizmann, T., 1915, **107**, 878), hydroxyanthraquinone (II), and fluoran (IV) series.

It is probable that when aluminium chloride is employed as a condensing agent, the products just quoted are accompanied



(I.)



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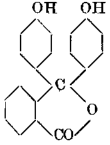
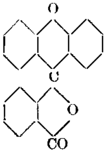


(III.)



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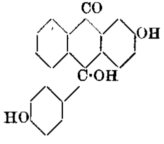
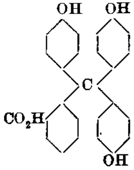
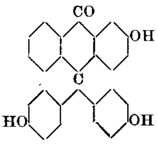


(V.)



(VI.)



(VII.)

by small quantities of substances belonging to the phenyloxanthranol (V), tetraphenylmethane-*o*-carboxylic acid (VI), and diphenylanthrone (VII) series (Copisarow, T., 1917, **111**, 10).

On replacing phthalic anhydride by phthalyl chloride, *iso*phthaleins or phenolic esters of phthalic acid are formed (Baeyer, *Ber.*, 1871, **4**, 659; Meyer, *Ber.*, 1891, **24**, 1414; 1893, **26**, 204; 1895, **28**, 431; Pawlewski, *Ber.*, 1895, **28**, 108, 2360; Limpricht, *Annalen*, 1898, **303**, 279; Csányi, *Ber.*, 1919, **52**, 1788).

In the course of the present investigation, it was found that:

(1) Hydrogen chloride, as a condensing agent, facilitates the formation of hydroxyanthraquinones and phthaleins.

(2) Boric acid, as a condensing agent, assists the formation, not only of *o*-ketonic acids and hydroxyanthraquinones (Deichler and Weizmann, *loc. cit.*), but also that of phthaleins and fluorans.

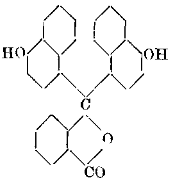
(3) Hydrogen chloride is most efficient in the presence of zinc chloride, and boric acid in the presence of concentrated sulphuric acid.

(4) The hydroxy-groups of the phthaleins are, as a rule, in the para-position, and of the fluorans in the ortho-position, with respect to the central carbon atom linking the phthaloyl with the phenolic gronps. This is proved by (*a*) the fact that phenolphthalein is not converted into fluoran on heating above its melting point or with concentrated snlphuric and boric acids; (*b*) the non-formation of 4:5-dimethylfluoran, *p*-cresolphthalein, and β-naphtholphthalein; (*c*) the fact that boric acid exercises in the case of termolecular reactions (fluoran formation) the same orientating effect as in the case of bimolecular reactions (Bentley, Gardner, and Weizmann, T., 1907, **91**, 1626); this is substantiated, not only by the constitution of the fluorans, but also by the fact that the *o*-ketonic acids are an intermediate stage in the formation of fluorans from phthalic anhydride, as in the case of phthalides (Pechmann, *Ber.*, 1881, **14**, 1865; Copisarow and Weizmann, *loc. cit.*).

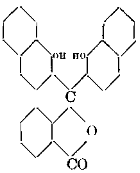
The apparently anomalous position of α-naphtholphthalein, prepared by the hydrolysis of di-1-ethoxynaphthylphthalide, in which Copisarow and Weizmann (*loc. cit.*) assigned the hydroxy-groups to the ortho-position with respect to the central carbon atom, on the ground that *o*-1-ethoxynaphthoylbenzoic acid can be regarded as an intermediate stage between phthalyl chloride and di-1-ethoxynaphthylphthalide, and also owing to the transformation of this α-naphtholphthalein into α-naphthafluoran, can now be easily explained.

Grabowski (*Ber.*, 1871, **4**, 661), and Sörensen and Palitzsch (*Biochem. Zeitsch.*, 1910, **24**, 384), have indicated the possible formation of two isomeric α-naphtholphthaleins, and considering

that (*a*) Grabowski's α-naphtholphthalein cannot be converted into α-naphthafluoran, thus differing from Copisarow and Weizmann's *o*-α-naphtholphthalein, and (*b*) the α-naphtholphthalein isolated by Csányi (*loc. cit.*) is identical with that of Copisarow and Weizmann (a sample preserved from 1915 and recrystallised twice from alcohol melted at 234—235°), there is no room for doubt that the following constitutions must be assigned to the two existing α-naphtholphthaleins:



(VIII.)
p-α-Naphtholphthalein.
(Grabowski.)



(IX.)
o-α-Naphtholphthalein.
(Copisarow and Weizmann, Csányi)

(5) Zinc chloride, as a condensing agent, is found to be superior to both concentrated sulphuric acid and stannic chloride, being more efficient than the former and more economical than the latter.

It was found that the alkali salts of the phthaleins, like those of phenols, are oxidised on prolonged keeping, especially on exposure to light or a current of air, giving dark, complex substances. The alkaline earth salts (barium, calcium, etc.) are less readily oxidised.

EXPERIMENTAL.

Zinc Chloride.

It was found that zinc chloride, prepared by evaporating to dryness a faintly acid solution of this salt, is a more efficient condensing agent than finely powdered fused sticks of zinc chloride. This superior quality is to be attributed to the fineness of division and presence of small quantities of hydrogen chloride rather than to the possible hydration of the unfused zinc chloride (compare aluminium chloride, Biltz, *Ber.*, 1893, **26**, 1960; Meyer, *Ber.*, 1896, **29**, 847), as the addition of small quantities of water to the fused zinc chloride not only does not add to, but actually diminishes, its efficiency.

Phenolphthalein (III).

Preparation by means of Concentrated Sulphuric Acid.—The condensation of phthalic anhydride with phenol in the presence of concentrated sulphuric acid was effected under the conditions given by Baeyer (*Annalen*, 1880, **202**, 69). It was found, however, that by employing an improved method of isolation and purification, the product contains about 5 per cent. of hydroxyanthraquinones. Baeyer's method of purification, consisting in pouring the decolorised alcoholic solution of the product into water, is thus ineffective. A more satisfactory method was found to be as follows.

The crude phenolphthalein, having been dissolved in aqueous sodium hydroxide and reprecipitated with hydrochloric acid, is dissolved in five times its weight of 65—70 per cent. methyl alcohol. The alcoholic solution is decolorised by boiling with animal charcoal and concentrated until solid begins to separate. On cooling and filtering, the first crop of phenolphthalein (yellow to white) is obtained; a second crop of this product is isolated on concentrating the filtrate. On further distillation, an orange-red, viscid oil separates, which, on keeping, solidifies to a brown, crystalline mass consisting of the two isomeric hydroxyanthraquinones and some phenolphthalein. The first two crops of phenolphthalein, when recrystallised from dilute alcohol, furnish snow-white crystals melting at 253°. This method of purification gives, not only phenolphthalein free from hydroxyanthraquinones, but also appears to be less wasteful than that of Baeyer, as more than 90 per cent. of the solvent is recovered. The separation of the two isomeric hydroxyanthraquinones from one another was effected according to Baeyer and Caro's method (*Ber.*, 1874, **7**, 969). The phenolphthalein accompanying the hydroxyanthraquinones is isolated by fractional crystallisation. The yield of pure phenolphthalein obtained by this method is 26 per cent. of that theoretically possible. The yield of fluoran (IV) (Baeyer, *Annalen*, 1882, **212**, 347) does not exceed 0·5 per cent.

Preparation by means of Concentrated Sulphuric and Boric Acids.—A mixture of 60 grams (1 mol.) of finely powdered phthalic anhydride, 80 grams (2 mols.) of phenol, 16 grams of concentrated sulphuric acid, and 8 grams of powdered boric acid was heated at 125—130° for eight hours. The product was poured into water, the mixture boiled to expel phenol, filtered white hot, and the brown residue washed with hot water. The residue was extracted several times with a 3 per cent. solution of sodium hydroxide, the extract cooled, and acidified with hydrochloric acid. The pre-

ipitate, which contained phenolphthalein and the hydroxyanthra- uinones, was purified as in the previous experiment. The residue, nsoluble in sodium hydroxide, crystallised from alcohol in white, hombic crystals melting at 173—175°, and consisted of fluoran. 'he yield of pure phenolphthalein was 31 per cent., that of fluoran per cent., and that of the hydroxyanthraquinones about 5 per ent. of the theoretical. No advantage was gained by employing oric anhydride instead of boric acid. The latter in the absence f concentrated sulphuric acid is ineffective as a condensing agent nder the conditions employed.

Preparation by means of Zinc Chloride.—The conditions of con- lensation were those described by Perkin and Kipping ("Organic 'hemistry," 1911, 654), the mixture being mechanically stirred. 'he method of purification of the products was identical with that lready described. The yield of pure phenolphthalein was 47 per ent., and that of the two hydroxyanthraquinones 6 per cent., of he theoretical. The yield of fluoran was negligible. When owdered fused zinc chloride was employed, instead of zinc chloride repared by the method described above, the yield of the products vas lowered.

Preparation by means of Hydrogen Chloride.—From analogy to he formation of esters, it was considered possible that hydrogen hloride might serve as a condensing agent for the production of hthaleins. Investigation showed that whilst hydrogen chloride y itself is not sufficiently effective, taken in conjunction with zinc hloride, a marked improvement in the yield of phenolphthalein, nd especially of the hydroxyanthraquinones, was observed. The ollowing table shows the results of condensation by means of dry ydrogen chloride.

Experi- ment.	Phthalic anhydride. Gram- mols.	Phenol. Gram- mols.	Period of heating, in hours.	Period of passing a current of hydrogen chloride, in hours.	Yield, per cent.	Colour.
1	1	2	6·0	0·5	0·2	greyish-brown
2	1	2	6·0	6·0	0·9	dark brown
3	1	4	6·0	6·0	0·8	"
4	1	2	24·0	24·0	1·7	"

These reactions were carried out at 120—125°, the method of solation and purification of the products being the same as in the xperiments already described. The ratio of phenolphthalein to he hydroxyanthraquinones was found to be approximately 1 to 1. No fluoran was found. When the temperature was raised to 170°, he proportion of the hydroxyanthraquinones and tarry matter was increased. The results indicate that (1) the yield of product

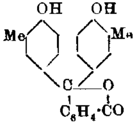
increases with the period of heating in a current of hydrogen chloride, and (2) the ratio of phenol to phthalic anhydride does not influence the yield.

These observations show a distinct difference between phthaleins and esters as regards the mechanism of their formation.

Preparation by means of Zinc Chloride and Hydrogen Chloride.—A current of dry hydrogen chloride was passed through a mixture of 60 grams of finely powdered phthalic anhydride, 70 grams of zinc chloride, and 80 grams of phenol at 120—125° for half an hour, the mixture being then heated for six hours at 120—125°. The product was poured into water, which was boiled to expel phenol. The mixture was then filtered hot, washed with hot water, and the yellowish-brown residue extracted several times with a warm 4—5 per cent. solution of sodium hydroxide. The deep red alkaline solution was cooled and acidified with hydrochloric acid, and the precipitate collected, pressed, and dried. The quantity of material insoluble in alkali did not exceed 0·5 per cent. The dried precipitate was purified by decolorising with animal charcoal and fractioual crystallisation from 65 per cent. methyl alcohol, as described in previous experiments. On concentrating the filtrate after the isolation of two crops of phenolphthalein, a brownish-red, viscid oil separated, which solidified on keeping. This contained hydroxyanthraquinones and phenolphthalein, the latter being about 33 per cent. of the total. The yield of pure phenolphthalein from the two crops was 52 per cent., and that of the hydroxyanthraquinones 21 per cent., the total yield of phenolphthalein being 59 per cent. of the theoretical; the 7 per cent. of phenolphthalein present in the oily residue was isolated only by a lengthy process of separation from the two hydroxyanthraquinones and fractional crystallisation, as already described. This fraction of phenolphthalein may therefore be disregarded in calculating the efficiency of this method of preparation. In subsequent experiments, the employment of hydrogen chloride was omitted.

When pure phenolphthalein is heated (*a*) above its melting point, or (*b*) with concentrated sulphuric and boric acids at 125—130° for eight hours, no fluoran is formed.

o-Cresolphthalein,

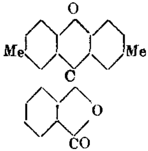


Baeyer (*Annalen*, 1880, **202**, 153) describes the employment of

tion of phthalic anhydride with *o*-cresol, but no indication is given either of the by-products formed or of the efficiency of each condensing agent. When phthalic anhydride was condensed with *o*-cresol in the presence of concentrated sulphuric acid under the conditions given by Baeyer, the yield was poor. A distinct improvement in yield, although this was still low, was achieved by using a mixture of concentrated sulphuric and boric acids. No 4:5-dimethylfluoran could be detected.

Preparation by means of Zinc Chloride.—Fifteen grams of phthalic anhydride and 25 grams of zinc chloride were finely powdered, 25 grams of *o*-cresol added, and the mixture was heated at 125° for eight hours. The product was worked up as in the previous experiments. On fractionally crystallising the crude precipitate from dilute alcohol, 16 grams (46 per cent. of the theoretical yield) of *o*-cresolphthalein were obtained in yellowish-white crystals melting at 216°. The last crop, fractionated by crystallising from acetic acid, was found to consist of 1-hydroxy-2-methylanthraquinone, melting at 184—185° (Bentley, Gardner, and Weizmann, T., 1907, **91**, 1634), 3-hydroxy-2-methylanthraquinone, melting at 262° (Baeyer, *Annalen*, 1880, **202**, 165), and a small quantity of *o*-cresolphthalein. No 2-hydroxy-1-methylanthraquinone could be detected. The combined yield of the two anthraquinones was about 4 per cent. of the theoretical.

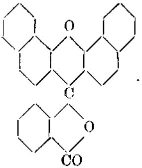
2:7-*Dimethylfluoran*,



The condensation of phthalic anhydride with *p*-cresol in the presence of zinc chloride was carried out in a manner similar to that employed in the case of *o*-cresol. The product, freed from *p*-cresol, phthalic acid, and zinc chloride, was extracted several times with dilute sodium hydroxide solution, and the dried residue decolorised with animal charcoal and crystallised from chloroform. It separated in yellowish-white crystals melting at 246°, and was identified as 2:7-dimethylfluoran (Baeyer, *Annalen*, 1882, **212**, 340). The brownish-red alkaline extract was acidified with hydrochloric acid, and the precipitate crystallised from glacial acetic acid in brownish-yellow needles melting at 169—170°, which were identified as 4-hydroxy-1-methylanthraquinone (Birukoff, *Ber.*,

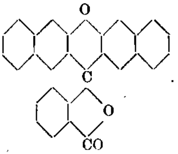
1887, **20**, 2069). The yield of 2:7-dimethylfluoran was 26 per cent., and that of 4-hydroxy-1-methylanthraquinone 2·5 per cent., of the theoretical. No trace of *p*-cresolphthalein could be detected.

p-α- *and* o-α-*Naphtholphthaleins* (VIII *and* IX) *and* α-*Naphthafluoran*,



Preparation by means of Zinc Chloride.—The condensation of phthalic anhydride with α-naphthol in the presence of zinc chloride results in the formation of *o*- and *p*-α-naphtholphthaleins, α-naphthafluoran, and small quantities of α-hydroxynaphthacenequinone. Five grams of phthalic anhydride, 10 grams of α-naphthol, and 15 grams of zinc chloride were finely powdered, thoroughly mixed, and heated in a flask immersed in an oil-bath at 100° for three hours. The product was extracted several times with boiling water, and then with a dilute solution of sodium hydroxide. The insoluble residue separated from benzene in small, white crystals melting at 300°, and was identified as α-naphthafluoran (Grabowski, *Ber.*, 1871, **4**, 661; Meyer, *Ber.*, 1893, **26**, 207; Deichler and Weizmann, *Ber.*, 1903, **36**, 548). The deep bluish-green, alkaline extract was fractionally precipitated with hydrochloric acid and carbon dioxide according to Werner's method (T., 1918, **113**, 20). The dried precipitate was extracted with benzene, from which, on keeping, brownish-yellow crystals melting at 209° separated. This substance was identified as *p*-α-naphthalphthalein (Grabowski, *Ber.*, 1871, **4**, 725; 1873, **6**, 1065). It gives a deep blue coloration with alkalis, and is not converted into α-naphthafluoran on heating above its melting point or with concentrated sulphuric and boric acids. On keeping the benzene mother liquors, a small quantity (about 1 per cent.) of α-hydroxynaphthacenequinone (Deichler and Weizmann, *loc. cit.*; D.R.-P. 134985) was isolated in orange-red needles melting at 303°. The residue left after extracting the precipitate with benzene dissolved in ethyl alcohol, from which it separated in pinkish-yellow, prismatic needles melting at 234—235°. This substance was identified as *o*-α-naphtholphthalein (Copisarow and Weizmann, *loc. cit.*;

Csányi, *loc. cit.*). It gives a deep green coloration (probably due to the *o*-quinonoid structure) with alkalis, and is converted into α-naphthafluoran on heating above its melting point or with concentrated sulphuric and boric acids. In this condensation, the yield of crude α-naphtholphthalein (dried precipitate) was 45 per cent., whilst that of α-naphthafluoran was 20 per cent., of the theoretical. The proportion of *p*-α- to *o*-α-naphtholphthalein is about 4 to 1. When the period of heating was reduced from three hours to one, the yield of crude α-naphtholphthalein was increased to 50 per cent., and that of α-naphthafluoran reduced to 17·3 per cent. The best yield was obtained by heating an intimate mixture of phthalic anhydride, α-naphthol, and zinc chloride in a shallow basin in an air-oven at 100° for half an hour. The yield of α-naphtholphthalein reached 59·3 per cent., and that of α-naphthafluoran 30 per cent., of the theoretical. Sörensen and Palitzsch (*loc. cit.*) obtained a 20·7 per cent. yield of α-naphtholphthalein by heating phthalyl chloride with α-naphthol, whilst Werner (*loc. cit.*), carrying out the condensation of phthalic anhydride with α-naphthol in the presence of concentrated sulphuric acid, found the yield to be 22·4 per cent. of the theoretical, the yield of α-naphthafluoran being very small.

β-Naphthafluoran, 

A mixture of 14·8 grams of phthalic anhydride, 30 grams of zinc chloride, and 28·8 grams of β-naphthol was heated for four hours at 100°. The product was extracted several times with boiling water and then with a hot dilute solution of sodium hydroxide. On acidifying the brownish-red, alkaline extract, a brown precipitate was obtained, which, owing to its minute quantity, could not be investigated. From analogy to other condensations, this precipitate was probably the corresponding quinone. The residue insoluble in alkalis, after being crystallised from acetic acid, melted at 293°, and was identified as β-naphthafluoran (Meyer, *Ber.*, 1891, **24**, 1414; 1893, **26**, 206). The yield was 12·5 per cent. of the theoretical, as compared with 7 per cent. obtained by Meyer.

The straight-line configuration for β-naphthafluoran may be accepted as the more probable one, for reasons similar to those

advanced in the case of phthaloyl- and diphthaloyl-carbazoles (Copisarow and Weizmann, *loc. cit.*).

The formation by α-naphthol of phthaleins which give intensely coloured sensitive alkaline salts, and the failure of β-naphthol to form a phthalein, may be used as a colour reaction for identifying small quantities of α-naphthol in β-naphthol.

The author wishes to express his thanks to Messrs. G. Greenwood and J. J. Sampey for assistance with the cresol condensations.

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[*Received, February 3rd*, 1920.]

XXVII.—*Certain Binary and Ternary Mixtures of Liquids having Constant Boiling Points.*

By WILLIAM RINGROSE GELSTON ATKINS.

IN the course of the distillation of commercial solvents for an industrial process, it was found necessary to study the possible mixtures of constant minimum boiling point afforded by the constituents. On examining the tables given by Young ("Fractional Distillation," pp. 67—69), and in subsequent literature, it was noticed that a number of combinations, which from their physical properties might be expected to furnish such mixtures, had not been investigated or had been examined only in a cursory manner. This work was accordingly undertaken, and the following systems were studied. The boiling points of the binary mixtures are shown under *AB*, of the ternary under *ABC*. A blank denotes that no mixture of constant boiling point is formed. Pressures are given in mm. of mercury, corrected to 0° under *P*.

At this stage, however, a copy of Lecat's exhaustive examination of such mixtures came into my hands, the work having been completed and published in Brussels in April, 1918, during the German occupation (Maurice Lecat, "La Tension de Vapeur des Mélanges de Liquides, L'Azéotropisme." Bruxelles: H. Lamertin. pp. 319).

It was found that all the binary mixtures given in this

A.	*B.*	*C.*	*AB.*	*ABC.*	*P.*
Acetone.	Carbon tetrachloride.	Water.	55·9°	—	763
Methyl ethyl ketone.	Carbon tetrachloride.	,,	73·8	65·7°	760
,, ,, ,,	*tert.*-Butyl alcohol.	,,	79·0	—	762
,, ,, ,,	*iso*Propyl alcohol.	,,	77·3	—	759
,, ,, ,,	*n*Propyl alcohol.	,,	—	—	
,, ,, ,,	Ethyl alcohol.	Ethyl acetate.	*	—	—
Methyl alcohol †	Carbon disulphide.	Water.	37·1	—	751
Carbon tetrachloride.	*tert.*-Butyl alcohol.	,,	71·0	64·7	768

* Already known.

† The addition of a little methyl alcohol to carbon tetrachloride will reveal the presence of carbon disulphide, present as an impurity, by the formation of the mixture boiling at 37·1°.

list had been studied, save *n*-propyl alcohol and methyl ethyl ketone. For all these, Lecat gives boiling points in good agreement with the figures shown here, save in the case of the mixture methyl ethyl ketone and *tert.*-butyl alcohol. For this, Lecat records that the binary mixture boils constantly at 77·5°, whereas the figure here given is 79·0°. This was obtained by adding to methyl ethyl ketone, boiling at 79·6°, 18 c.c. of the tertiary alcohol. Boiling began at 74·8°, and became constant for four observations at 79·0—79·05° at fifty-eight to twenty-eight drops per minute.

No attempt was made to analyse the binary mixtures of constant boiling point, since Lecat had done this.

Of the ternary mixtures, the only one examined by Lecat, so far as could be ascertained, was that containing carbon tetrachloride, *tert.*-butyl alcohol, and water, for which no details are given. This mixture and the corresponding one, with methyl ethyl ketone replacing alcohol, were therefore analysed.

To weighed quantities of the two major components, small weighed quantities of water were added, and the mixtures distilled up to the middle point between the boiling point of the ternary and the binary mixtures of constant boiling point in each case. It was assumed that all the water had passed over below this temperature, but this is not strictly accurate, as turbidity was still visible at the top of the distillation column near the side-tube. The quantity of carbon tetrachloride was then determined by measuring the volume it occupied after extraction of the distillate with water to remove the ketone and alcohol respectively. The latter were estimated by difference, but in the case of the ketone a direct estimation was also made by Messinger's method, adopting the usual precautions, and those advocated by Collischonn (*J. Soc. Chem. Ind.*, 1891, **10**, 166) for acetone. The constant used was that 1 c.c. of *N*/10-iodine solution is equivalent to 0·00114 gram

of methyl ethyl ketone. The following are the compositions of the ternary mixtures of constant boiling point:

	Per cent.	Per cent.
Carbon tetrachloride	85·0	74·8
tert.-Butyl alcohol (by difference)	11·9	—
Methyl ethyl ketone (by difference)	—	22·2
,, ,, ,, (Messinger)	—	20·1*
Water	3·1	3·0

* It is probable that the extraction of the ketone from the chloride was not quite complete, although a large quantity of water was used.

In every case, the distillations were conducted with an electric hot plate suitably screened with asbestos board. The thermometers had been corrected at the Reichsanstalt in 1913. An eight-section Young evaporator still-head was used throughout, for the loan of which, for the use of the chemicals, and for his advice, I am indebted to Prof. S. Young. I wish also to acknowledge my indebtedness to the Chemical Society for a grant for the purchase of chemicals, and to Prof. H. H. Dixon for permission to carry out the work in the School of Botany.

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DUBLIN. [*Received, January 29th*, 1920.]

XXVIII.—*The Estimation of Nitrogen in Nitrocellulose and Inorganic Nitrates with the Nitrometer.*

By ERNEST GEORGE BECKETT.

THE estimation of nitrogen in inorganic and organic nitrates by means of the nitrometer is based on the reaction which occurs when a solution of the nitrate in concentrated sulphuric acid is shaken with mercury. This reaction may be represented by the following equation:

$$3H_2SO_4 + 2HNO_3 + 6Hg = 3Hg_2SO_4 + 2NO + 4H_2O.$$

The volume of nitric oxide evolved according to this equation is a measure of the quantity of nitrogen present as nitrate, and it is assumed for the purpose of calculation that the gas obtained is pure nitric oxide, and that all, and only the nitrogen present as nitrate or nitrite, has been converted into gas.

It has been known for some time that these assumptions are not correct, and hence, if the method gives trustworthy results, it can only be by a compensation of errors. Several factors have been found to exercise considerable influence on the course of the reac-

tion, and thus it is essential that the method should be standardised as far as possible. Thus Marqueyrol and Florentin (*Bull. Soc. chim.*, 1911, [iv], **9**, 234) found that prolonged shaking causes a diminution of volume by reduction of the nitric oxide gas, and also a re-absorption of some of the nitrogen by the sulphuric acid. This cause of error becomes negligible if the shaking is not unduly prolonged and if the concentration of the acid is not too high.

This reaction also occurs if the nitrometer is allowed to stand after the evolution of gas has taken place, but in that case the reaction is very slow. In an experiment with guncotton and 96·8 per cent. acid, the original volume of 109·95 c.c. became 109·80 c.c. after standing for twenty-six and a-half hours. On the other hand, the time which elapses before the mixture of mercury, sulphuric acid, and nitrocellulose has been shaken, but after the two latter substances have been introduced into the nitrometer, was found to have a marked influence on the results. This fact was discovered in the analytical laboratory of Messrs. Nobel's explosives factory at Ardeer in 1914, when the war caused a large increase in the number of nitrocelluloses to be analysed, and thus rendered almost unavoidable a certain amount of delay in carrying out the analyses.

Table I shows the influence of the time factor and of the concentration of the acid on the results at this stage of the method.

TABLE I.

Determination of nitrogen in guncotton with various strengths of sulphuric acid and the effect of allowing the mixture to stand before being shaken.

Sulphuric acid.	Interval between introducing the guncotton and acid into the nitrometer and shaking being				
Per cent.	No time.	¼ hour.	½ hour.	1 hour.	17–20 hours.
99·87	12·63	—	—	11·76	—
	12·50	—	—	11·82	—
96·80	12·94	—	—	12·74	10·14
	12·945	—	—	12·68	10·28
	12·93	—	—	—	10·71
	12·96	—	—	—	—
94·0	12·975	13·065	—	13·04	11·90
92·5	12·73	13·04	13·035	13·015	12·69
	12·57	—	—	—	—

The influence of the same factors on the estimation of nitric acid is given in table II. The results given in this table with 93·3 per cent. acid were obtained with pure sodium nitrate, and those with

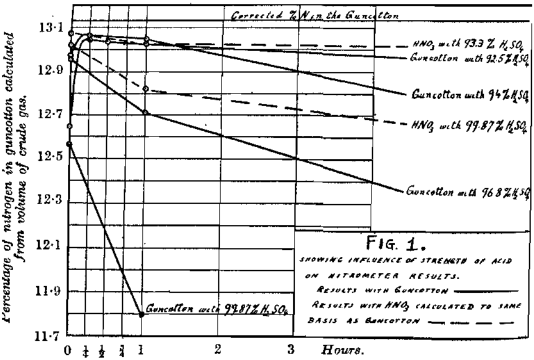
the more concentrated acid with a mixture of nitric and sulphuric acids.

TABLE II.

Determination of nitrogen in nitric acid with various strengths of sulphuric acid and the effect of allowing the mixture to stand in the nitrometer before being shaken.

Sulphuric acid.	Interval between introducing the mixture into the nitrometer and shaking being		
Per cent.	No time.	1 hour.	17 hours.
99·87	2·081	2·058	1·948
	2·098	—	—
93·3	16·38	16·31	16·298
	16·38	16·32	—

The results of both tables are shown graphically in Fig. 1. It will be noticed that the effect of time and concentration of acid



Interval between introducing guncotton and acid into nitrometer and shaking.

was much less in the absence of organic matter, but the influence of allowing the mixture to remain, even with 93·3 per cent. acid, is quite noticeable, and that with the stronger acid is quite marked.

Marquerol and Florentin found that the highest figures were obtained with 94 per cent. acid, but this result was not confirmed by experiments (not published) carried out by chemists in explosives works. It was generally found that 96—97 per cent. acid

gave the highest results, and thus it came about that this strength of acid is that most generally used for nitrometer work.

Neither Marquerol and Florentin nor the other chemists who investigated the question were apparently aware of the importance of the time which elapses between the introduction of the guncotton into the nitrometer and the shaking, and the discrepancies in the results may be accounted for by this.

Table I shows that the highest figures were obtained with the weaker acids, but only if a sufficient interval was allowed to elapse before shaking. If the nitrometer was shaken immediately after the guncotton was introduced, higher results were obtained with 96·8 per cent. acid than with 92·5 per cent. acid.

It is clear from these results that it is preferable to work with a weaker acid, as the results are less influenced by the time factor than they are with the stronger acid; but the most important question is to determine which results represent most closely the true nitrogen content.

Marqueyrol and Florentiu, by comparing the nitrometer method with Schlœsing's method, found that the former gave correct results, but it is unsafe to determine the trustworthiness of one method by comparison with another equally unproven method.

In a previous communication (*J. Soc. Chem. Ind.*, 1914, **33**, 628), the author attacked the problem in another way, and found that with guncotton and 96 per cent. acid the various errors balance one another, and that therefore the results were correct. This statement was supported by the analysis of the gas and the estimation of the nitrogen in the sulphuric acid residues by Kjeldahl's method.

It has been found since that Kjeldahl's method in this case does not show all the nitrogen—that some of the nitrogen in the residual sulphuric acid is not converted into ammonia on heating, but is given off in the form of nitrogen or nitrous oxide.

As the conclusion previously drawn must have been wrong, owing to a part of the nitrogen having escaped detection, it was decided to repeat the work on a more elaborate scale, and, so far as possible, to test every method of analysis employed with the view of discovering any source of loss.

This research deals principally with the estimation of nitrogen in nitrocelluloses, and the great difficulty was the determination of the true nitrogen content. There is no method known of ascertaining this simply and accurately. The method adopted was the same as that used in the previous investigation, namely, (1) the analysis and measurement of the gas ovolved; (2) the analysis of the sulphuric acid residues. As the nitrometer estimation is carried

out in a closed glass vessel sealed by mercury, the nitrogen entering in the form of nitrocelluloses must, after the experiment, be either in the gas or in the acid, as it may be taken for granted that it cannot be absorbed in any quantity by the mercury. Besides the nitrogen introduced into the nitrometer as nitrocellulose, a small quantity enters in the form of dissolved gaseous nitrogen in the sulphuric acid. If, then, the gas is accurately analysed and measured, and all the nitrogen in the sulphuric acid residue correctly estimated, the quantity of nitrogen in the nitrometer is correctly known, and by subtracting the nitrogen introduced by the sulphuric acid, the actual quantity of nitrogen in the nitrocellulose can be calculated. This method of procedure has the advantage that the results show to what the discrepancies in the estimation by the nitrometer are due.

In this paper, the methods adopted for the analysis of the gas and the residual acid are described in Part I, and the actual experimental figures obtained are given and discussed in Part II.

Part I.

Methods of Analysis.

Analysis and Measurement of the Gas.—The gas was transferred from the nitrometer to a gas-analysing apparatus similar in principle to that recommended by Bone and Wheeler, but specially designed for the particular requirements of the case. The gas may contain, besides a large quantity of nitric oxide, small quantities of sulphur dioxide, carbon dioxide, nitrous oxide, nitrogen, and carbon monoxide. The analysis was carried out in the following order:

(1) Absorption of sulphur dioxide and carbon dioxide.

(2) Absorption of nitric oxide.

(3) Absorption of carbon monoxide.

As the gas is evolved in the dry state in the nitrometer, it was measured dry. Great difficulty was experienced in attempting to do this at first, but by washing the measuring vessel before use with 75 per cent. sulphuric acid and leaving one or two drops of it in the vessel, the results became more satisfactory. A more concentrated sulphuric acid was not used, as nitric oxide reacts with concentrated sulphuric acid and mercury, and a weaker acid could not be used, as the vapour tension becomes too high. The vapour pressure of 75 per cent. sulphuric acid being about 0·7 mm. at the ordinary temperature, the true dry volume of the gas was taken as being 999/1000 of that measured. As the carbon dioxide and sulphur dioxide were absorbed by dry sodium hydroxide, the volume

was also measured dry after these gases had been eliminated. After absorption of the nitric oxide by ferrous chloride solution, the residual gas was measured wet, and as the volumes of gas dealt with at this stage of the analysis were comparatively small, no appreciable error was incurred in neglecting the vapour tension. In order to avoid a constant drying of the apparatus, one part was used exclusively for measuring the dry gas and another part only for the latter portion of the analysis. The gas was first transferred from the nitrometer into a gas-measuring vessel, which was immersed in water, kept stirred by a stream of air being bubbled through it, and measured dry after having been brought to atmospheric pressure.

Estimation of the Carbon Dioxide and Sulphur Dioxide.—Owing to the possibility of carbon dioxide and sulphur dioxide being absorbed by the reagents used for eliminating the nitric oxide, these were estimated first. Alkali hydroxides are stated to react with nitric oxide, and this was found to be, indeed, the case with solid potassium hydroxide. Solid sodium hydroxide, however, was found to have no influence, as the following figures show.

TABLE III.

Showing the action of nitric oxide on potassium hydroxide.

	Volume of gas at N.T.P. in c.c.	Difference in c.c.
Original volume	110·36	—
After one hour over KOH	109·22	1·14
After another hour over KOH the latter having been moistened	109·08	0·14
After another hour	108·59	0·49
,, ,,	107·90	0·69
,, ,,	107·22	0·68

The large diminution in volume which occurred at first was due to the presence of carbon dioxide and sulphur dioxide in the gas. The gas was then allowed to act on a stick of solid sodium hydroxide.

TABLE IV.

Showing the action of nitric oxide on sodium hydroxide.

	Volume of gas at N.T.P. in c.c.	Difference in c.c.
Original volume	107·11	—
After one hour over NaOH	107·09	0·02
After another hour over NaOH which had been slightly moistened	107·16	−0·07
After another hour and a half	107·13	0·03
After two hours over a stick of calcium chloride	107·08	0·05

In the actual analysis, the gas was allowed to remain for two to three hours in contact with the stick of sodium hydroxide. The latter was tested on several occasions for nitrites and nitrates by Devarda's method, in order to ascertain if any nitrogen was abstracted from the gas by this treatment, but no appreciable quantity could be found.

Estimation of the Nitric Oxide.—The gas, after absorption of the carbon dioxide and sulphur dioxide, consisted mainly of nitric oxide, and contained also small quantities of carbon monoxide, nitrogen, and nitrous oxide. The latter gas, owing to its great solubility in most solutions, gave much trouble, but a concentrated solution of ferrous chloride seemed to be specially suited for separating nitrous oxide from nitric oxide, as the solubility of the former gas in it was found to be about 16 per cent. at the ordinary temperature. Altogether, 9 c.c. of ferrous chloride solution were generally used for absorbing the nitric oxide, and this solution could have absorbed 1·4 c.c. of nitrous oxide. Under the conditions of the experiment, however, it was found by a trial with a synthetic mixture that not more than 0·34 c.c. was absorbed during the analysis of a mixture containing 9 c.c. of nitrous oxide and 109 c.c. of nitric oxide. When the quantity of nitrous oxide was much smaller, as was usually the case, the loss must have been much less.

In the actual analysis, the gas was treated with 7 c.c. of concentrated ferrous chloride solution until no further diminution of volume occurred. It was then treated with 0·5 to 0·75 c.c. of the same solution for one to two hours at ordinary atmospheric pressure. Very little diminution occurred as a rule during this last treatment. The gas was then immediately measured. Washing with water is not permissible, as the solubility of nitrous oxide at the ordinary temperature is about 80 per cent. by volume. It was found that even with the small quantities of gas usually dealt with at this stage of the analysis, treatment with 2 c.c. of water caused a loss of 0·3 c.c., although the gas contained a large proportion of nitrogen and its volume was only about 1 c.c.

Estimation of Carbon Monoxide.—The solubility of nitrous oxide in ammoniacal cuprous chloride was found to be about 30 per cent. by volume, that is, twice that in ferrous chloride. Moreover, treatment with ammoniacal cuprous chloride has always to be followed by a treatment with water or dilute acid to absorb the ammonia left in the gas. This double treatment caused such an appreciable loss of nitrous oxide that the use of this absorbent for carbon monoxide had to be avoided. Acid cuprous chloride was found to be no better.

An attempt was made to analyse the mixture by keeping the gas over a heated mixture of copper oxide and copper. The carbon monoxide would be oxidised to carbon dioxide, and the nitrous oxide reduced by the copper to nitrogen. This method was found to work quite well if the gas was kept for half an hour in contact with the mixture at 250°. One treatment was found to be sufficient when the gas was poor in carbon monoxide, but when the latter was present to the extent of 50 per cent. or more, two treatments were necessary.

The copper was prepared by precipitation from a solution of copper chloride with a rod of pure zinc. Copper sulphate could not be used for this purpose, as the product then contains small quantities of copper sulphide. The copper oxide was first prepared by igniting copper nitrate, but it was found that the ordinary copper oxide, as used for combustions, made by igniting copper wire, was just as suitable.

A mixture of about equal parts of these two substances was placed in a glass bulb having a little more than twice the volume of the gas to be analysed, and the bulb connected to the gas-measuring apparatus by a glass capillary tube and an indiarubber tube connexion. Before each experiment, a small piece of fresh filter paper was inserted in the capillary tube to absorb any liquid which it was difficult otherwise to prevent from being drawn into the bulb. The bulb and contents were then heated in an oil-bath to 250—280° and exhausted. The gas to be analysed was admitted, heated for an hour, and pumped out again. The volume was then measured, the carbon dioxide absorbed, and the volume measured again. The diminution represented the volume of carbon monoxide. As the proportion of the latter gas was small, by adopting the procedure described, incomplete exhaustion of the bulb before the treatment had no effect on the results, and even if a trace of the gas had been left in the bulb after treatment, the accuracy of the analysis was not appreciably impaired.

No attempt was made to ascertain the proportion of nitrous oxide to nitrogen in the nitrometer gas. They were both classed together, as they contain the same quantity of nitrogen per c.c.

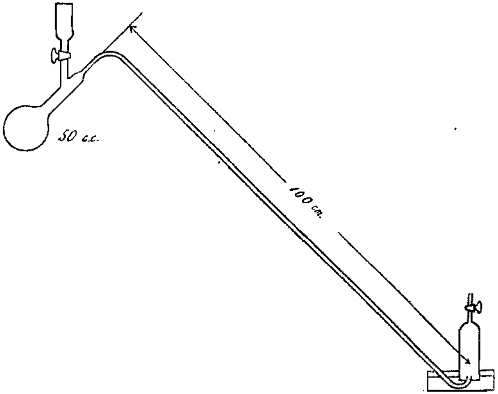
Estimation of the Nitrogen in the Sulphuric Acid Residues.

Estimation of the Gases Evolved on Heating.—A flask of the shape shown in Fig. 2 was filled with mercury, care being taken that no air was left adhering to the sides of the vessel. It was then inverted, with the end of the long tube dipping in a trough of mercury. By this means, a Torricellian vacuum was produced

in the vessel, which contained no appreciable quantities of permanent gas.

The sulphuric acid residue was transferred from the nitrometer to the funnel, and allowed to be drawn into the vessel, care being taken that no air was sucked in with it. The nitrometer was washed with two quantities of 5 c.c. of sulphuric acid, which were also transferred to the flask in the same way. The flask was gently heated, as in a Kjeldahl estimation, and the sulphur dioxide produced by the action of the mercury which had been left in the stopper of the apparatus and had been sucked in, together with

FIG. 2.



the sulphuric acid, swept out all the other gases in a comparatively short time. The gases were collected over 20 c.c. of a 30 per cent. solution of potassium hydroxide, and consisted in the case of guncotton mainly of carbon monoxide with a little nitrogen and nitrous oxide. The acid from an analysis of an inorganic substance gave only nitrogen and nitrous oxide. It is curious that nitric oxide was never found in these gases in appreciable quantities, although the sulphuric acid must have been saturated with the gas when it was in the nitrometer. The mercury dissolved in the sulphuric acid is in the form of mercurous sulphate in the nitrometer, but after the acid has been heated, the mercurous sulphate

is converted into mercuric sulphate. No doubt the nitric oxide is reduced at the higher temperature by the mercurous sulphate to nitrogen or nitrous oxide.

After the evolution of gas had almost ceased, which occurred when the drop of mercury had dissolved, the sulphuric acid was heated to boiling until the liquid appeared transparent, but not necessarily colourless. Experiment showed that heating until colourless, and heating for several hours after the acid had become colourless and after the addition of potassium sulphate, had no effect on the amount of ammonia formed in the sulphuric acid.

The gas collected over the potassium hydroxide, which in the case of nitrocellulose usually amounted to 2 to 3 c.c., was transferred to the wet gas analysis apparatus, and the carbon monoxide removed by heating over copper and copper oxide and treatment with sodium hydroxide. In this case, where the quantity of carbon monoxide was very much greater than that of the nitrogen gases, the actual residue of nitrogen was measured, and not the diminution in volume on treatment with potassium hydroxide, as described above.

Experiments were carried out in order to ascertain whether the 20 c.c. of potassium hydroxide dissolved an appreciable quantity of nitrous oxide, which would thus escape detection. A concentrated sulphuric acid was prepared containing a known volume of dissolved nitrous oxide in solution. A weighed quantity of this acid was subjected to the same treatment as the sulphuric acid residues from the nitrometer estimations, and the volume of gas obtained was only 0·11 c.c. short of that which the acid contained. This experiment represents an extreme case, as the quantity of the gas was greater than that usually found, and it consisted of pure nitrous oxide, whereas in the actual analysis of nitrocellulose acid, the proportion of nitrous oxide in the gas must have been less than 25 per cent.

The potassium hydroxide after an experiment with nitrocellulose was examined for nitrates and nitrites by Devarda's method, but none could be found. Blank experiments were always carried out with the same quantities of the same sulphuric acid as used in the actual analysis, and the results obtained in these really represent the quantity of gas dissolved in the sulphuric acid. In the blank experiments, however, the gas contained also a small quantity of oxygen, which had to be removed with alkaline pyrogallol solution.

Estimation of Ammonia formed in the Acid.—The sulphuric acid after it had been boiled until transparent was transferred to a round-bottomed litre flask, and after adding an excess of sodium

hydroxide and sufficient sodium sulphide to convert all the mercur present into sulphide, the ammonia was distilled off into a know quantity of $N/100$-acid. The acid was then titrated with $N/10($ sodium hydroxide.

Blank determinations were always carried out with the sam quantities of the same sulphuric acid, sodium hydroxide, sodiun sulphide, and water as in the actual analysis.

Many attempts were made here also to ascertain if any loss o nitrogen occurred.

The ammonia distillation was carried out with the addition o Devarda's alloy and other reducing agents in a variety of way without increasing the result.

The distillation of ammonia was also carried out under diminishec pressure, and the evolved gases were collected, but the quantity o gas so obtained, namely, 0·29 c.c., was not much greater than that given off in a blank determination, namely, 0·20 c.c.

The addition of sodium sulphide was found to be essential.

PART II.

Discussion of Results Obtained.

The following are the details of the nitrometric method which was used for obtaining the results given in this paper. The method is similar to that used in many explosive factories.

The nitrometer was first washed out with concentrated sulphuric acid, and the cup washed with distilled water and dried.

Dried and sieved nitrocellulose (0·5—0·55 gram) was placed in a weighing bottle and heated to 96° in a steam-bath for one hour. The weighing bottle was then accurately weighed, the nitrocellulose dropped into the cup of the nitrometer, and the empty weighing bottle weighed again. Five c.c. of the sulphuric acid of specified strength were added to the cup, the nitrocellulose was stirred in the acid with a glass rod, and run into the nitrometer. The cup was then washed with successive quantities of 2·5 c.c., 2·5 c.c., and 5 c.c. of the same acid, and these were run into the nitrometer as well. The whole operation of washing the nitrocellulose into the nitrometer with the 15 c.c. of acid occupied five minutes. After the introduction of the acid and nitrocellulose, the nitrometer was allowed to stand for the specified time and then vigorously shaken for one and a half minutes. It was allowed to stand for ten minutes, again shaken vigorously for one minute, and the gas transferred to the measuring vessel described above.

The sodium nitrate was introduced into the nitrometer cup in

TABLE V.

Giving analyses of the various products of nitrometer determinations.

Substance used.	Sulphuric acid. Per cent.	Interval between introducing guncotton and acid into the nitrometer and shaking.	Substance used. Grams.	Analysis of gas. NO. c.c.	Analysis of gas. CO_2 and SO_2. c.c.	Analysis of gas. CO. c.c.	Analysis of gas. N_2 and N_2O. c.c.	Analysis of residual acid. N_2 and N_2O evolved as gas. c.c.	Analysis of residual acid. NH_3 formed in acid as c.c. NO.	N_2 in acid used for analysis. c.c.	Nitrogen calculated from volume of crude gas. Per cent.	Corrected nitrogen content Per cent.	Correction to be added to percentage of nitrogen from crude gas.
[illegible]pont high [n]itrogen gun[c]otton.	96·8	None	0·51135	106·76	0·25	0·25	0·82	0·59	1·16	0·39	13·21	13·44	0·23
	96·8	None	0·50965	106·27	0·30	0·25	0·85	0·62	1·20	0·39	13·195	13·45	0·255
[Gu]ncotton. ...	96·8	None	0·54865	111·81	0·64*	0·22	0·82	0·485	1·20	0·39	12·93	13·085	0·155
	96·8	None	0·5263	107·69	0·47*	0·17	0·80	0·50	1·13	0·39	12·96	13·14	0·18
[Sl]ightly soluble [n]itrocellulose.	96·8	None	0·54415	109·03	0·21	0·16	0·63	0·58	0·89	0·39	12·64	12·82	0·18
	96·8	None	0·53975	107·94	0·15	0·21	0·66	0·59	0·94	0·39	12·62	12·81	0·19
[...]sting soluble [n]itrocellulose.	96·8	None	0·55575	104·65	0·22	0·26	0·95	0·68	1·16	0·39	11·93	12·18	0·25
	96·8	None	0·55155	104·37	0·22	0·25	0·73	0·635	1·12	0·39	11·965	12·18	0·215
[Pu]re sodium [n]itrate (Kahl-[b]aum).	96·8	None	0·4513	117·70	0·11	—	0·48	0·35	0·15	0·39	16·382 =99·48% $NaNO_3$	16·447 =99·90% $NaNO_3$	0·065
	96·8	None	0·45265	118·09	0·03	—	0·50	0·40	0·08	0·39	16·382 =99·48% $NaNO_3$	16·459 =99·97% $NaNO_3$	0·077
[Gu]ncotton ...	99·87	None	0·52525	102·23	1·10	0·23	1·49	0·72	4·75	0·62	12·50	13·115	0·615
	96·8	20 hours	0·5294	76·43	2·29	1·30	10·70	2·06	8·83	0·39	10·71	12·9	2·19
	92·5	None	0·5316	105·86	0·26	0·08	0·65	—	3·28	0·30	12·57	—	—
	92·5	½ hour	0·5228	107·72	0·60	0·16	0·53	0·45	0·98	0·30	13·04	13·14	0·10
[So]dium nitrate	96·8	17 hours	0·4509	116·37	0·20	—	0·98	0·38	0·27	0·39	16·30	16·44	0·14
[N]itric acid dissolved in sulphuric acid.	99·87	None	2·867	95·08	0·45	—	0·75	0·67	0·07	0·62	—	—	—
	99·87	17 hours	3·140	91·79	2·19	—	3·27	1·94	1·29	0·62	—	—	—

* Other results for the determination of carbon dioxide in the gas from guncotton were also obtained, but they were not added to the table as the analyses were not completed. These results for a similar quantity of gas were 0·57, 0·57, 0·40, 0·59, 0·56 c.c.

the same way as the guncotton, but it was then dissolved in two portions of water of 0·5 c.c. each, which were run into the nitrometer, and the cup was washed with 96·8 per cent. sulphuric acid as described above. In this case, the addition of the water reduced the concentration of the acid to 93·3 per cent.

The results are given in table V.

The results for the various kinds of nitrocellulose under the same conditions show that they act in the nitrometer in the same way under normal conditions with 96·8 per cent. acid; the only essential difference observed was the quantity of carbon dioxide and sulphur dioxide in the gas evolved from guncotton. This difference is not caused by any special behaviour of the guncotton itself, but by the presence of calcium carbonate, as the following figures show.

TABLE VI.

Giving percentage of calcium carbonate in the nitrocelluloses used.

	$CaCO_3$. Per cent.	CO_2 from 0·53 gram. c.c.
Dupont high nitrogen guncotton ...	0·02	0·025
Guncotton	0·25	0·29
Highly soluble nitrocellulose	0·02	0·025
Blasting soluble nitrocellulose.........	0·06	0·07

Taking the figures as a whole, it will be seen that under all the conditions examined, the results calculated from the crude gas with both inorganic and organic nitrates were too low. The best result for guncotton was obtained with 92·5 per cent. acid and an interval of fifteen minutes between the introduction of the guncotton and acid into the nitrometer and the shaking. It will also be observed that the best results are concomitant with a high degree of purity of the gas and, at the same time, a small content of nitrogen in the residues. With guncotton, the purest gas is obtained with 92·5 per cent. acid, and no interval between the introduction of the nitrocellulose and the shaking; but in this case a large amount of nitrogen is retained by the acid, due, apparently, to incomplete decomposition of the guncotton.

The table also shows that the errors in the case of inorganic nitrates are smaller than they are with nitrocelluloses; hence the standardisation of the nitrometer with pure sodium or potassium nitrate does not necessarily eliminate the errors of the determination of nitrogen in organic nitrates.

The use of the more dilute sulphuric acids is advisable, not only on account of the better results obtained, but also because they generally contain a smaller quantity of dissolved nitrogen.

Nitrogen appears to dissolve in a greater degree the more con-

centrated the acid between the limits of 90 and 100 per cent.; hence more dissolved nitrogen is usually found in the more highly concentrated acids, as the figures in table VII show. These figures have been calculated from the blank experiments mentioned on p. 229.

TABLE VII.

Dissolved nitrogen in concentrated sulphuric acid.

Sulphuric acid. Per cent.	Percentage of nitrogen by volume.
99·87	3·09
96·8	1·56
94·0	1·11
92·5	0·98

The nitrogen from the sulphuric acid is partly driven out during an estimation by the escaping nitric oxide, and is thus partly responsible for the content of nitrogen in the latter gas.

The separate estimation of nitrogen and nitrous oxide in the nitric oxide was not carried out in the above analyses, as these two gases contain the same quantity of nitrogen per c.c. In two cases, however, this was determined by combustion with hydrogen. The crude nitric oxide was obtained by shaking guncotton with 96 per cent. sulphuric acid, after allowing the mixture to remain in the nitrometer for about twenty-four hours. In one case this gas contained 4·6 per cent. of nitrogen and 6·8 per cent. of nitrous oxide; in the other experiment, the gas was found to contain 5·8 per cent. of nitrogen and 5·6 per cent. of nitrous oxide.

The large quantity of gas evolved on heating the residual sulphuric acid in some of the experiments described in table V was explained by the great solubility of nitrous oxide in concentrated sulphuric acid, which was found to be about 58 per cent. by volume at the ordinary temperature.

Influence of the Quantity of Sulphuric Acid.

The question of the influence of the quantity of sulphuric acid used is of importance, as many firms, especially those in America, use 50 c.c. of 94—94·5 per cent. sulphuric acid and the Lunge volumenometer, instead of 15 c.c. as in the ordinary nitrometer. Apparently the larger quantity of acid is used to accelerate the decomposition, which with a smaller quantity of this strength of acid might remain incomplete unless a sufficient interval were allowed between the introduction of the guncotton and the shaking. The larger quantity of nitric oxide dissolved in the acid is com-

TABLE VIII.

Giving results obtained with 50 c.c. of 94 per cent. sulphuric acid.

Substance used.	No. of expt.	Substance. Gram.	Crude gas at N.T.P. c.c.	Nitrogen calculated from crude gas. Per cent.	Nitrogen in acid used for analysis c.c.	Composition of gas.	Composition of acid.	Corrected content of nitrogen cal. as c.c. NO.	Corrected nitrogen content. Per cent.
Guncotton	1	0·5253	108·09	12·86	0·71	From No. 2. $NO = 106{\cdot}48$ c.c.	From No. 2. N_2 and N_2O as gas $= 0{\cdot}94$ c.c.	110·40	13·15
	2	0·52485	108·06	12·87		SO_3 and $CO_2 = 0{\cdot}32$ c.c. $CO = 0{\cdot}13$ c.c.	NO present as ammonia $= 1{\cdot}20$ c.c.		
	3	0·52545	108·35	12·89		N_2 and $N_2O = 1{\cdot}13$ c.c.			
	Mean.	—	—	12·87		—	—	—	13·15
Pure sodium nitrate	4	0·4511	117·52	16·29	0·71	From No. 7. $NO = 116{\cdot}50$ c.c.	—	—	—
	5	0·4497	116·93	16·255		$SO_2 = 0{\cdot}04$ c.c.	—	—	—
	6	0·4459	115·87	16·245					
	7	0·44975	117·23	16·29		N_2 and $N_2O = 0{\cdot}69$ c.c.	—	—	—
	Mean	—	—	16·27					

pensated by standardising the measuring apparatus with pure potassium nitrate. The results obtained with 50 c.c. of 94·0 per cent. acid are given in table VIII.

The results show that the ammonia formed in the residual acid is the same as with a smaller quantity of a similar acid, but that all the other sources of error are greater; hence the actual volume of gas obtained is smaller than with the ordinary nitrometer, and even standardisation with potassium or sodium nitrate does not produce results any higher or truer than those obtainable with the ordinary nitrometer.

It may be mentioned here that in the experiments with sodium nitrate, the addition of 1 c.c. of water to 50 c.c. of 94 per cent. acid produced an acid of about 93 per cent., that is, practically the same as that obtained in the other experiments with sodium nitrate, where 15 c.c. of 96·8 per cent. acid were diluted with 1 c.c. of water.

Conclusion.

The general result of the research is that the nitrometric estimation of nitrogen in nitrocelluloses invariably gives results which are too low.

It has been found that the interval of time which is allowed to elapse between the introduction of the nitrate and sulphuric acid into the nitrometer and the shaking has a great influence on the results in the case of nitrocelluloses. The effect is less in the case of inorganic nitrates.

The truest results are obtained by using 15 c.c. of 92·5—94·0 per cent. sulphuric acid, and by allowing a quarter to half an hour to elapse between the introduction of the nitrocellulose and acid into the nitrometer and the shaking. In this case, the error is about 0·7 per cent., taking the nitrogen as 100.

This research was carried out in the Research Laboratories of Nobel's Explosives Co., Ardeer, and I wish to express here my thanks to Mr. J. Rogers, O.B.E., and to Mr. W. Rintoul, O.B E., for their kind permission to publish the results.

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XXIX.—*The Preparation of Methylamine from Ammonium Methyl Sulphate.*

By William Smith Denham and Lionel Frederick Knapp.

Werner (T., 1914, **105**, 2762), who observed that methylamine is produced when ammonium methyl sulphate is heated, followed acidimetrically the progress of the change to temperatures up to 275°, and regards it as being represented essentially by the equation $NH_4 \cdot SO_4Me = NH_3Me \cdot SO_4H$, although at temperatures above 240° a small quantity of ethylene is formed owing to a subsidiary reaction. He records the separation under favourable conditions of an 85·6 per cent. yield of methylamine. The methyl sulphates of the substituted ammonium bases behave similarly when heated, and the discoverer suggests that those reactions may be found of practical value for the preparation of the substituted methylammonium bases.

The results now communicated, obtained in an investigation of Werner's reaction undertaken with the object of utilising it for the preparation of methylamine, indicate that, under the conditions observed, the reaction is less simple than represented above, and that, at any temperature at which a noticeable transformation of ammonium methyl sulphate occurs, a mixture is produced containing ammonium, methylammonium, dimethylammonium, trimethylammonium, and (probably) tetramethylammonium salts, as, indeed, is implied in Werner's statement that "the further progress and limit of the isomeric transformation may be expressed by the general equations:

$$NH_2RR' \cdot SO_4Me = NHRR'Me \cdot SO_4H$$
$$NHRR'R'' \cdot SO_4Me = NRR'R''Me \cdot SO_4H,"$$

for, once some methylamine is produced, the melted mass may be considered, as pointed out by Werner, to contain methylamine methyl sulphate among other salts.

It is evident that the formation of secondary and tertiary amines need not become apparent in the acidimetric values, since, as indicated by equations given below, an interconversion of the amines may cause no alteration in the amount of free acid present. The products of the transformation were therefore separated approximately, and from these analyses it is concluded that, by heating ammonium methyl sulphate alone, about 25 to 30 per cent. of the ammonia can be converted into methylamine. When the period of heating is prolonged, the proportion of dimethylamine

ınd trimethylamine (taken together) in the product increases, but he absolute amount of methylamine does not alter very much.

Methylamine is produced when a mixture of the sulphate of .mmonium, dimethylamine, and trimethylamine is heated, and this upports the view that in the melted mass obtained by heating ımmonium methyl sulphate, a state of equilibrium is attained or ıpproximated to in which, as expressed by the equations

$$2NH_3Me\cdot SO_4H \rightleftharpoons NH_4\cdot SO_4H + NH_2Me_2\cdot SO_4H,$$
$$2NH_2Me_2\cdot SO_4H \rightleftharpoons NH_3Me\cdot SO_4H + NHMe_3\cdot SO_4H,$$

alts of methylamine and ammonium are opposed. The addition of ammonium salts to the ammonium methyl sulphate may there-'ore be expected to increase the yield of methylamine, an expecta-·ion which is in accordance with the fact. When one equivalent of ammonium sulphate was mixed with ammonium methyl sulphate, ı distinct improvement was observed in the yield of methylamine, ɔut the mixture does not melt very readily, and, possibly on ıccount of the imperfect fusion, the yield was not further increased vhen two equivalents of ammonium sulphate were added. Of the 'ew other ammonium salts which it appeared to be practicable to ıse, ammonium benzenesulphonate was chosen. With ammonium nethyl sulphate, this salt forms an easily fusible mixture, from vhich a greatly increased yield of methylamine is obtained, whilst he proportion of dimethylamine and trimethylamine produced 'taken together) is greatly diminished.

The possibility that the beneficial effect of the presence of ımmonium benzenesulphonate may be related to the known methyl-ıting action of methyl benzenesulphonate was not investigated; ılthough this possibility might account for an increased yield of nethylamine, it does not explain the alteration in the relative ɔroportions of methylamine on the one hand and dimethylamine ınd trimethylamine on the other if we suppose the subsequent ransformations to be reversible. No further sulphonation of the ɔenzene residue was observed, and the improved yield cannot there-'ore be ascribed to a partial removal in this way of free sulphuric ıcid, the presence of which, indeed, does not appear to be harmful ınd is probably necessary.

The employment of gaseous ammonia suggests itself as a means of neutralising the free acid (supposing that desirable) and of supplying at the same time an increased concentration of ımmonium salts, and an improved yield of methylamine was indeed ɔbtained when ammonia in regulated amounts was admitted to the reaction vessel, but the method is inconvenient. At the ordinary :emperature, ammonia reacts with ammonium methyl sulphate

with the evolution of heat, probably owing to the occurrence of the following or some similar reaction,

$$NH_4 \cdot SO_4Me + NH_3 = NH_4 \cdot SO_3 \cdot NH_2 + MeOH,$$

and no methylamine is produced.

It is concluded that, to obtain the best yield of methylamine by means of Werner's reaction, the ammonium methyl sulphate should be heated for one hour and a-half at 260° or at a slightly higher temperature, when the yield of methylamine is about 27 per cent. of the theoretical yield; when a mixture of ammonium methyl sulphate with two equivalents of ammonium benzenesulphonate is heated under conditions otherwise the same, the yield of methylamine is nearly 50 per cent. of the theoretical.

Experimental.

In most of the experiments summarised in the following tables, 1/10th gram-molecule (12·9 grams) of ammonium methyl sulphate contained in a test-tube was heated in an oil-bath. Excess of sodium hydroxide was added to the aqueous solution of the product, and the liberated bases were distilled, usually under diminished pressure, into aqueous hydrochloric acid. The hydrochloric acid solution of the amines was then evaporated, at first on the water-bath under atmospheric pressure, and finally in a vacuum until the weight was constant. The dried mass was extracted twice by boiling with absolute alcohol, using 50 c.c. of alcohol for the first extraction and 25 c.c. for the second, and the residue of ammonium chloride was washed with 25 c.c. of cold alcohol. (When very large quantities of ammonium salts were present, a preliminary extraction was made with much alcohol, and the residue from the evaporation of the solution thus obtained was then extracted as above.) After removing the alcohol by distillation from the united alcoholic extracts and washings, the residual mixture of ammonium chloride and amine hydrochlorides was dried until constant in weight, and in some experiments this residue was extracted twice by boiling it with chloroform, using 50 c.c. of the solvent each time. According to Bresler (*Ann. Chim. anal.*, 1901, **6**, 28; compare Behrend, *Annalen*, 1884, **222**, 119), methylamine hydrochloride is insoluble in hot chloroform, whilst the hydrochlorides of dimethylamine and trimethylamine dissolve quite readily. When ammonium chloride alone was boiled with 50 c.c. and 25 c.c. of alcohol successively, the united extracts gave on evaporation 0·55 gram of ammonium chloride, and in the calculation of the "yield of methylamine" from the weight of the alcoholic extract, 0·55 gram has been deducted as an approximate

correction for the ammonium chloride present. The "yield" thus found is employed merely as a conventional method of comparing the results of experiments when more accurate methods of comparison are not available, for the alcoholic extract contained the hydrochlorides of dimethylamine and trimethylamine, and probably more ammonium chloride than was allowed for. The residue from the extraction with chloroform contained, besides methylamine hydrochloride, the ammonium chloride present in the alcoholic extract, and in calculating the "yield of methylamine" from the quantity of product dissolved by alcohol, but undissolved by chloroform, the same weight (0·55 gram) was first deducted. In several experiments, the proportion of methylamine in the residue from the extraction with chloroform was determined by François' method (*Compt. rend.*, 1907, **144**, 857), that is, by fixing the ammonia with yellow mercuric oxide and titrating the methylamine in the filtrate.

In each of the experiments of which the results are summarised in this table, a tube containing 20 grams of ammonium methyl sulphate was placed in an oil-bath already heated to the desired temperature and removed after thirty minutes, the contents of the tube being at the maximum temperature for periods varying between fifteen and twenty minutes. Two-fifths of the product (derived from 8 grams of ammonium methyl sulphate) were used for titration, and from the remainder the amine hydrochlorides were prepared and extracted with alcohol, as described above. Although the part of the product treated in this way was derived from only 12 grams of ammonium methyl sulphate, the same approximate correction was made for the ammonium chloride present as in the experiments in which 12·9 grams were used, since the same quantities of alcohol were employed in the extractions. Werner's results by titration after fifteen minutes' heating at nearly equal temperatures are given for comparison. The "yields of methylamine" are expressed as percentages of the theoretical yield if complete transformation occurred. The weight of methylamine hydrochloride from 12 grams of ammonium methyl sulphate would then be 6·27 grams.

Effervescence occurred in all cases, especially in 3 and 4, where the temperatures in the tubes rose above that of the bath, but both the effervescence and the evolution of heat slackened after a few minutes. The fused products from experiments 1 and 2 were slightly yellow; those from 3 and 4 were dark reddish-brown.

TABLE I.

No. of experiment.	I. Total duration of heating Minutes.	I. Period at maximum temperature.	II. Amine hydrochlorides dissolved by alcohol (grams).	III. Yield of methylamine calculated from III after correction for NH_4Cl.	IV. Yield of methylamine from titration.	V. "Isomeric change" at nearly equal temperatures (Werner).
				Per cent. of theoretical yield.		
1	30	16 min. at 160—165°	0·61	1·0	2·2	11·5 (160°)
2	30	18 ,, 200—205°	1·17	10·0	23·8	25·8 (200—205°)
3	30	22 ,, 255—260°	3·94	54·1	89·6	85·9 (250—260°)
4	30	22 ,, 274—275°	4·19	58·1	95·6	97·2 (275°)

Table II.

In the experiments summarised here, the period of heating was longer. 12·9 Grams of ammonium methyl sulphate were used for each experiment, the theoretical yield of methylamine hydrochloride being 6·75 grams.

The temperatures are those of the bath, initially at the ordinary temperature.

No. of experiment.	I. Duration of heating. Hours.	I. Temperature, etc.	II. Weight of amine hydrochlorides dissolved by alcohol. Grams.	III. Yield of methylamine calculated from II after correction for ammonium chloride. Percentage of the theoretical yield.
5	100	100°	0·69	2·1
6	7	5 hours up to 168°. 2 hours at 160—168°.	0·70	2·2
7	6½	2 hours up to 206°. 4½ hours at 196—206°.	3·24	39·9
8	6	3 hours up to 255°. 3 hours at 230—255°.	3·89	49·5
9	1⅔	1 hour up to 272°. ⅔ hour at 240—272°.	4·52	58·8

Partial Solubility of the Amine Hydrochlorides in Chloroform.—Table III shows the proportion of the alcohol-soluble product.

Table III.

12·9 Grams of ammonium methyl sulphate were heated in each experiment, the theoretical yield of methylammonium chloride being 6·75 grams.

No. of experiment.	I. Duration of heating. Mins.	I. Temperature.	II. Weight of amine hydrochlorides dissolved by alcohol. Grams.	III. Weight of amine hydrochlorides dissolved by alcohol but undissolved by chloroform. Grams.	IV. Yield of methylamine calculated from II after correction for ammonium chloride. Percentage of the theoretical yield.	V. Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of the theoretical yield.
10	18	230—234°	3·0	2·1	36·3	23·0
11	17	254—258°	3·74	2·44	47·3	28·0
12	16	From room temperature to 260°	3·47	2·62	43·3	30·1

found to be insoluble in chloroform. The results are confirmed by those displayed in later tables. In experiments 10 and 11, the vessels containing the ammonium methyl sulphate were placed in an oil-bath already heated to the required temperature. In experiment 12, the ammonium methyl sulphate was heated in sixteen minutes from the ordinary temperature to 260°, and then removed from the bath, when the temperature of the melted salt remained at about 260° for a minute or two, and then fell slowly.

Nitrogen in the Still Residue.—In experiment (10), after the volatile bases had been removed by prolonged distillation of the alkaline solution of the product obtained on heating the ammonium methyl sulphate, the residue in the distillation flask was neutralised with sulphuric acid and evaporated to dryness. The dried residue was found to contain nitrogen.

Effect of Ammonia on the Transformation.—In experiment (13) (table IV), a very slow current of ammonia was passed into the salt after it had been melted and heated to 170°; in experiment (14), the flask containing the salt was heated rapidly to 220°, and then attached to a reservoir of ammonia gas under a pressure of 100 mm., in addition to the atmospheric pressure; and in experiments (15), (16), and (17), ammonia, similarly under a slightly increased pressure, was present from the beginning. If the yield of methylamine were theoretical, and if all the acid formed were neutralised by ammonia, the total weights of hydrochlorides in column III would be 12·1 grams (5·35 grams of ammonium chloride and 6·75 grams of methylamine hydrochloride).

TABLE IV.

12·9 Grams of ammonium methyl sulphate were heated in each experiment. The oil-bath and contents were heated from the ordinary temperature. The temperatures are those of the bath.

	I.		II.	III.	IV.
No. of experiment.	Duration of heating. Hours.	Temperature.	Weight of amine hydrochlorides. Grams.	Weight of amine hydrochlorides dissolved by alcohol. Grams.	Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of the theoretical yield.
13	3¼	1¼ hours at 234°	8·89	4·32	55·9
14	3¼	2 ,, 260°	7·13	4·93	64·9
15	3½	2 ,, 260°	7·48	5·14	68·0
16	2¾	2 ,, 240°	11·27	4·59	59·9
17	[illegible]	2 ,, 260°	12·15	4·52	58·6

Effect of Ammonium Sulphate on the Transformation.—Table V summarises the results of a study of the effect on the yield of methylamine of the duration of heating and of the presence during the reaction of different proportions of ammonium sulphate. In this series, the percentage of methylamine was determined by François' method, already referred to, in that portion of the amine hydrochlorides which was dissolved by alcohol, but undissolved by chloroform.

Estimation of the Dimethylamine and Trimethylamine in the Chloroform-soluble Part.—The following percentages of dimethylamine and trimethylamine hydrochlorides were found in the chloroform-soluble portions obtained in experiments 19 and 24, using Bertheaume's method (*Compt. rend.*, 1910, **150**, 1251), that is, by precipitating the trimethylamine as periodide and estimating volumetrically the trimethylamine in the precipitate and the dimethylamine in the solution:

	Dimethylamine hydrochloride. Per cent.	Trimethylamine hydrochloride. Per cent.
Chloroform-soluble portion from experiment 19	67·4	64·8
Chloroform-soluble portion from experiment 24	27·0	31·6

Although the comparison is not complete, since in experiment 28 the percentage of methylamine in the chloroform-insoluble portion was not estimated, the results tabulated above indicate that two equivalents of ammonium benzenesulphonate are as effective as four. With the larger proportion of ammonium benzenesulphonate, the mixture did not fuse so readily.

Examination of the Residual Benzenesulphonate.—In experiment 25, the amines were liberated by the addition of baryta, the excess of which was removed from the residue in the distilling flask after the distillation by means of carbon dioxide. The solution was then evaporated to dryness, and the barium estimated in the dried product.

Found: Ba=30·7.

$(C_6H_5\cdot SO_3)_2Ba$ requires Ba=30·4, and $C_6H_4(SO_3)_2Ba$ requires Ba=36·7 per cent.

General Comparison of Experiments made at about 260°.—In table VII are assembled those experiments in which ammonium methyl sulphate was heated for different periods at about 260°, with and without the addition of ammonia or of an ammonium salt. Two experiments made in closed vessels (29 and 30) are included.

TABLE V.

12·9 Grams of ammonium methyl sulphate were heated in each experiment. One equivalent of ammonium sulphate = 1/20 mol. = 6·6 grams. Experiments 18—23 were made simultaneously, using the same oil-bath, which was heated from the ordinary temperature. The temperatures are those of the bath.

No. of experiment.	I. Weight of ammonium sulphate added. Grams.	II. Duration of heating. Hours.	II. Temperature.	III. Weight of amine hydrochlorides dissolved by alcohol. Grams.	IV. Weight of amine hydrochlorides dissolved by alcohol but undissolved by chloroform. Grams.	V. Percentage of methylamine hydrochloride by analytical estimation in substance (col. IV) undissolved by chloroform.	VI. Yield of methylamine calculated from III after correction for ammonium chloride. (Percentage of theoretical yield.)	VII. Yield of methylamine calculated from IV after correction for ammonium chloride. (Percentage of theoretical yield.)	VIII. Yield of methylamine by analytical estimation of methylamine (IV and V). (Percentage of theoretical yield.)
18	None	$1\frac{1}{2}$	$\frac{3}{4}$ hour at 260°	4·57	2·74	66·1	59·6	32·4	26·8
19	6·6	$1\frac{1}{2}$	,,	4·99	3·14	70·5	65·8	38·4	32·8
20	13·2	$1\frac{1}{2}$	,,	4·81	3·01	61·7	63·1	36·4	27·5
21	None	3	$2\frac{1}{4}$ hour at 260°	4·54	2·63	68·2	59·1	30·8	24·0
22	6·6	3	,,	4·49	3·02	70·5	58·3	36·3	31·5
23	13·2	3	,,	4·74	2·95	68·6	62·1	35·6	30·0
24	66·0 (10 equivalents)	2	1 hour at 260°	4·39	2·89	69·2	56·9	34·7	29·6

Effect of Ammonium Benzenesulphonate on the Transformation.

TABLE VI.

12·9 Grams of ammonium methyl sulphate were heated in each experiment, except in experiment 25, where 6·45 grams were used and other substances in proportion. The figures shown in the table for experiment 25 are the actual figures multiplied by two to facilitate comparison. One equivalent of ammonium benzenesulphonate = 17·5 grams.

No. of experiment.	I. Weight of ammonium benzene-sulphonate added. Grams.	II. Duration of heating.	II. Temperature.	III. Weight of amine hydro-chlorides dissolved by alcohol. Grams.	IV. Weight of amine hydro-chlorides dissolved by alcohol but undissolved by chloroform. Grams.	V. Percentage of methylamine by analytical estimation in substance (col. IV) undissolved by chloroform.	VI. Yield of methylamine calculated from III after correction for ammonium chloride. (Percentage of theoretical yield.)	VII. Yield of methylamine calculated from IV after correction for ammonium chloride. (Percentage of theoretical yield.)	VIII. Yield of methylamine by analytical estimation of methylamine (IV and V). (Percentage of theoretical yield.)
25	17·5	1½ hours	Heated from ord. temp. 20 min. at 250—260°.	4·82	3·68	—	63·3	46·4	—
26	35·0	1½ "	Heated from ord. temp. 55 min. at 250—260°.	5·02	4·35	75·5	66·2	56·3	48·7
27	35·0	18 min.	Ammonium methyl sulphate added to ammonium benzenesulphonate already heated to 250—260°.	4·52	3·89	—	58·8	49·5	—
28	70·0	1½ hours	Heated from ord. temp. 1 hour at 250—260°.	5·24	4·29	—	71·0	55·4	—

TABLE VII.

I.		II.		III.	IV.	V.	VI.
				Yield of methylamine as percentage the theoretical yield.			
No. of experiment.	Addition.	Duration of heating.	Temperature.	From titration.	From amine hydrochloride soluble in alcohol after correction for ammonium chloride.	From amine hydrochloride soluble in alcohol but insoluble in chloroform after correction for ammonium chloride.	By analytical estimation of the methylamine.
12	None.	16 min.	ord. temp. to 260°.	—	43·3	30·1	—
11	,,	17 ,,	254—258°.	—	47·3	28·0	—
3	,,	30 ,,	22 min. at 255—260°.	89·6	54·1	—	—
18	,,	1½ hours.	45 min. at 260°.	—	59·6	32·4	26·8
29	None (closed vessel).	1½ ,,	1 hour at 250—260°.	—	58·5	33·3	—
21	None.	3 ,,	2¼ hours at 260°.	—	59·1	30·8	24·6
14	Ammonia.	3½ ,,	2 hours at 260°.	—	64·9	—	—
15	,,	3 ,,	2 hours at 260°.	—	68·0	—	—
19	1 equivalent $(NH_4)_2SO_4$.	1½ ,,	45 min. at 260°.	—	65·8	38·4	32·8
30	1 equivalent $(NH_4)_2SO_4$ (closed vessel).	1½ ,,	45 min. at 260°.	—	56·0	34·8	—
22	1 equivalent $(NH_4)_2SO_4$.	3 ,,	2¼ hours at 260°.	—	58·3	36·3	31·5
20	2 equivalents $(NH_4)_2SO_4$.	1½ ,,	45 min. at 260°.	—	63·1	36·4	27·5
23	,, ,,	3 ,,	2¼ hours at 260°.	—	62·1	35·6	30·0
24	10 equivalents $(NH_4)_2SO_4$.	2 ,,	1 hour at 260°.	—	56·9	34·7	29·6
25	1 equivalent $C_6H_5{\cdot}SO_3NH_4$.	1½ ,,	20 min. at 250—260°.	—	63·3	46·4	—
27	2 equivalents $C_6H_5{\cdot}SO_3NH_4$.	18 min.	255—260°.	—	58·8	49·5	—
26	,, ,,	1½ hours.	55 min. at 250—260°.	—	66·2	58·3	48·7
28	4 equivalents $C_6H_5{\cdot}SO_3NH_4$.	1½ ,,	1 hour at 250—260°.	—	71·0	55·4	—

Methylamine from a Mixture of the Sulphates of Ammonium, Dimethylammonium, and Trimethylammonium.—Five grams of the mixed hydrochlorides of dimethylamine and trimethylamine, obtained in the extractions with chloroform, were mixed with an excess of sodium hydroxide solution, and the liberated bases were distilled into an aqueous solution of 6 grams of sulphuric acid. The solution was neutralised with ammonia (but the presence of some free acid would doubtless have been advantageous), and the residue, after evaporation to dryness, was heated at 270° for a short time. The bases were converted into the hydrochlorides and extracted with alcohol, and then with chloroform, which dissolved 1·55 grams. After purification of the portion insoluble in chloroform, 0·44 gram of methylamine hydrochloride was obtained.

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XXX.—*The Behaviour of the Constituents of Banded Bituminous Coal on Coking. Studies in the Composition of Coal.*

By RUDOLF LESSING.

THE four main constituents of banded bituminous coal have been isolated and described by Stopes (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 470) mainly from the microscopical and palæobotanical point of view, and designated by her fusain, durain, clarain, and vitrain respectively. These four ingredients, derived from the Thick Coal, Hamstead Colliery, have been chemically investigated recently by Tideswell and Wheeler (T., 1919, **115**, 619). Their researches comprised proximate and ultimate analysis, the action of solvents and of reagents on the four substances, and their destructive distillation in a vacuum with examination of the gaseous and liquid products. This vacuum distillation was carried out under conditions which yielded in each instance, not a coherent coke, but a solid residue consisting of loose particles little different in outward appearance from the original materials, although shrunk in total volume.

At the suggestion of Drs. Stopes and Wheeler, I investigated the behaviour of samples of fusain, durain, clarain, and vitrain upon coking in an apparatus previously described by me (*J. Soc. Chem.*

Ind., 1912, **31**, 465, 671; *Trans. Inst. Gas Eng.*, 1912, 242; see also *J. Gas Lighting*, 1912, **118**, 815, 855). The method consists briefly in placing 1 gram of the coal sample into a cylindrical silica retort of approximately 1·25 cm. internal diameter and fitted with a side-tube 6·5 cm. from the bottom, and heating it in an electric furnace. A loosely fitting piston weighing 7·5 grams is placed on the coal charge, compressing it slightly, while allowing the gases and vapours to escape freely. These are led through the side-tube and a cotton-wool scrubber into a eudiometer.

Tideswell and Wheeler heated each sample for several days, raising the temperature by only 50° at a time in order to remove completely every trace of gas or liquid volatile at each stage of decomposition. The great difference in my procedure from theirs is that, apart from the coal being heated in a confined space, the whole period of carbonisation extends over a few minutes only, and that there is a considerable temperature gradient from the outside to the interior of the coal, at any rate during the first minute or two, which permits the re-condensation of some primary products of decomposition and their reaction with coal which has not yet undergone any considerable thermal change. By this reaction of an original or partly carbonised coal with primary products and the secondary decomposition of the latter, a coherent coke is formed.

This fundamental difference of the working conditions must be borne in mind when comparing the quantities and properties of products obtained by Tideswell and Wheeler with those found in this research.

The investigation was principally directed to ascertain any distinctions exhibited by the solid coking residues of the four coal constituents. The yields of liquid and gaseous products at the two temperatures employed, namely, 600° and 900°, were, however, also determined.

The samples originally submitted were fine powders passing through a 200-mesh screen. As was to be expected, the gas space between the particles of such powders was not sufficient to permit of the gas readily disengaging itself, especially during the evolution of the large volumes generated during the initial distilling period. It was therefore found that a few seconds after inserting the retort into the hot furnace a certain portion of coal dust was thrown up beyond the piston, passing between it and the retort wall, thus escaping carbonisation in the relatively cool upper part of the retort. This portion of the sample was finally weighed as carbon, producing a corresponding deficiency in the coke, tar, and gas figures. The small quantity of coal substance extracted from this

PLATE A.

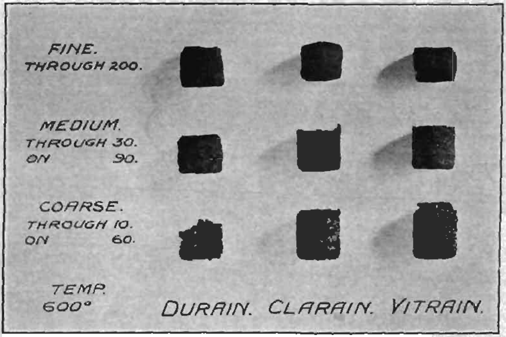
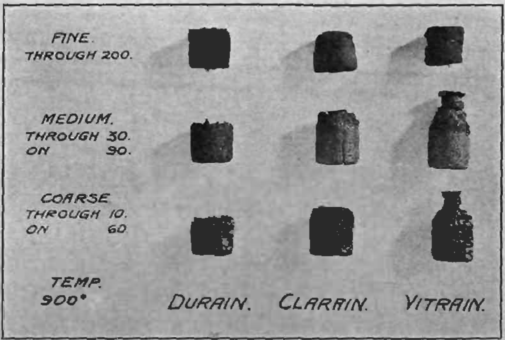


PLATE B.



4/5 Natural size.

[To face p. 249.

portion with chloroform, and consequently weighed as tar, was regarded as negligible.

In order to avoid this drawback, another set of samples (except fusain, which was obtained almost exclusively as powder), which *had been crushed to pass through 10 mesh and remain on 60 mesh*, was kindly supplied by Dr. Wheeler. For the purpose of avoiding the fairly large spaces formed by the cohesion of these particles along comparatively few lines of contact, a third series of samples was prepared by crushing these specimens to a size passing through 30 mesh and remaining on 90 mesh. This size contained spaces large enough to allow free escape of gas, and left the solid particles in closer aggregate. These showed a higher sintering or agglutination effect, even under the slight pressure of the silica piston and with the short period of complete carbonisation, which are insignificant when compared respectively with the weight of superimposed coal, say, in a gas retort or coke-oven and with the duration of a large-scale charge, which may take as many hours or more as minutes are required in this test.

The results of the two series of experiments are recorded in tables I and II. The gas-production curves are shown in Figs. 1 and 2, and it should be noted that the volumes plotted could not be corrected for N.T.P. Photographs of the coke residues obtained are shown in 4/5 natural size in plates *A* and *B*.

Coke Residues.—The distinctive physical character of the coke obtained from the different specimens under varying conditions is the most interesting and important outcome of this research. The differences between fusain, durain, clarain, and vitrain already observed by Stopes and Wheeler are shown here in an accentuated form. The differences exhibited by the coke specimens from the four substances are not less remarkable than the consistency of properties observed with each one of them under varying conditions of size and heating. This constancy is even observable in details which appear somewhat obscured in the photographs, and particularly with the "fine" specimens.

Fusain.—Fusain shows no outward change in appearance after coking. It has no tendency whatever to adhere, and the solid coking residue is therefore a powder, like the original specimen. The particles retain their fibrous structure and dull black colour. No differences in appearance are observable between residues obtained at 600° and 900°.

Durain.—Durain undergoes practically no change of form during coking. The particles retain their angular shape and show little tendency to adhere to each other, although more than fusain. This applies particularly to the 600° series, and it was found impossible

to preserve a complete coke cylinder from the coarse specimen for photography. In several attempts, portions of the coke crumbled away, as shown in the photograph. At 900° the coke specimens are somewhat firmer, but in general durain must be regarded as practically devoid of any "coking value." The colour of the coke is the same dull, greyish-black as that of the original durain.

Clarain.—Clarain showed considerable fusion and merging of particles. At 900° most of the fine and medium-sized particles lost their identity almost completely, whilst even the coarse ones sintered or fused to rounded shapes which firmly cohered or fluxed together with their immediate neighbours. A peculiarity, which may or may not be significant, is that all clarain cokes made at 900° had a vertical crack which made them appear as of ellipsoid cross-section. They also showed a tendency to "mushroom" formation, which was, however, not as definite as in the vitrain specimens. All clarain cokes showed a peculiar brown sheen.

Vitrain.—The vitrain particles were well sintered and showed rounding of the angular edges, but the consolidation of particles did not go so far as with clarain. The colour is a silver-white of high lustre. The coke specimens from vitrain were the most distinctive in shape. This was of the "mushroom" type previously described (*loc. cit.*). It was remarkably definite at 900°, whilst the tendency of the lifting effect can be clearly seen on the specimens from the 600° tests. This phenomenon, which has not been observed in the use of other coking methods, is probably closely connected with the whole problem of the carbonisation of coal and the as yet unexplained discrepancy in the behaviour of various coals when subjected to thermal decomposition. As a plausible explanation, it is suggested that the formation of coke is due to the partial or complete fusion of coal or solutions of coal in tar or pitch primarily produced from adjacent coal particles, followed by an energetic thermal decomposition of the fused or sintered mass, by which its chemical constitution is altered, and further fusion is consequently arrested. According to the composition and the physical character of a coal or a coal constituent, these phases may follow each other in more or less rapid sequence, or may overlap very considerably.

In the case of vitrain, it appears that the phase of rigidity follows so rapidly after the fusion phase or overlaps it to such an extent that an impermeable wall is formed round the coal cylinder before the heat has penetrated to the inner core. As soon as this occurs and gasification proceeds, the gas pressure, overcoming the weight of the piston, throws up the core with explosive force in the only direction in which movement is possible. The pressure

having been released, the semi-rigid eruption is forthwith completely solidified, whilst the porosity of the whole specimen increases sufficiently for the ready release of the gas made during the remainder of the carbonising period. It is interesting to note that

TABLE I.

Temperature, 600°.

	Original Coals.			
	Fusain.	Durain.	Clarain.	Vitrain.
	Coarse :	Through 10 mesh on 60 mesh.		Per cent.
Coke		71·38	60·16	62·21
Carbon		—	0·46	0·29
Coke + Carbon		71·38	60·62	62·50
Tar		9·13	10·44	10·00
Gas (N.T.P.)		73 c.c.	96 c.c.	83 c.c.
	Medium :	Through 30 mesh on 90 mesh.		
Coke		71·18	60·18	62·21
Carbon		—	0·84	0·27
Coke + Carbon		71·18	61·02	62·48
Tar		8·38	11·46	10·75
Gas (N.T.P.)		76 c.c.	90 c.c.	81 c.c.
	Fine :	Through 200 mesh.		
Coke	—	—	—	—
Carbon	—	—	—	—
Coke + Carbon	81·42	67·22	65·36	65·80
Tar	3·56	8·35	8·86	5·88
Gas (N.T.P.)	64 c.c.	73 c.c.	80 c.c.	80 c.c.

	Ash-free Dry Coals.			
	Fusain.	Durain.	Clarain.	Vitrain.
	Coarse :	Through 10 mesh on 60 mesh.		
Coke		83·16	69·36	72·39
Carbon		—	0·53	0·34
Coke + Carbon		83·16	69·89	72·73
Tar		10·64	12·04	11·64
Gas (N.T.P.)		85 c.c.	111 c.c.	97 c.c.
	Medium :	Through 30 mesh on 90 mesh.		
Coke		82·92	69·38	72·39
Carbon		—	0·97	0·31
Coke + Carbon		82·92	70·35	72·70
Tar		9·76	13·21	12·51
Gas (N.T.P.)		89 c.c.	104 c.c.	94 c.c.
	Fine :	Through 200 mesh.		
Coke	—	—	—	—
Carbon	—	—	—	—
Coke + Carbon	87·51	76·28	75·18	76·57
Tar	3·83	9·48	10·19	6·84
Gas (N.T.P.)	69 c.c.	83 c.c.	92 c.c.	93 c.c.

the eruption can be observed by the shock given to the tar vapours in the retort tube.

The phenomenon was also observed, but less markedly, at 600°, and to a still less degree with clarain.

TABLE II.

Temperature, 900°.

Original Coals.

	Fusain.	Durain.	Clarain.	Vitrain.
	Coarse:	Through 10 mesh on 60 mesh.		Per cent.
Coke		65·74	54·34	54·66
Carbon		2·58	0·62	0·56
Coke + Carbon		68·32	54·96	55·22
Tar		8·56	10·40	11·10
Gas (N.T.P.)		182 c.c.	206 c.c.	209 c.c.
	Medium:	Through 30 mesh on 90 mesh.		
Coke		62·56	54·06	54·96
Carbon		2·06	0·60	0·66
Coke + Carbon		64·62	54·66	55·62
Tar		9·92	11·38	12·58
Gas (N.T.P.)		190 c.c.	217 c.c.	221 c.c.
	Fine:	Through 200 mesh.		
Coke	—	—	—	—
Carbon	—	—	—	—
Coke + Carbon	77·84	61·88	56·28	56·88
Tar	3·86	7·28	10·82	13·00
Gas (N.T.P.)	207 c.c.	184 c.c.	206 c.c.	194 c.c.

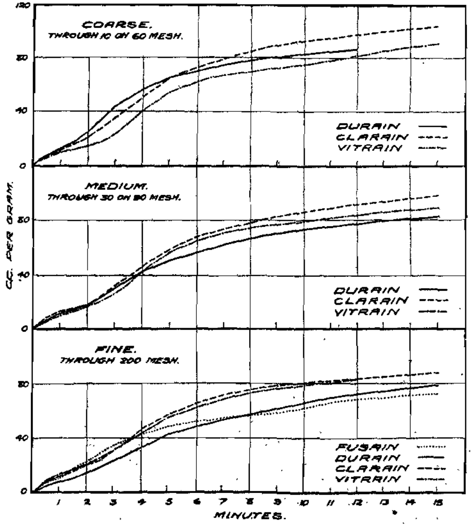
Ash-free Dry Coals.

	Fusain.	Durain.	Clarain.	Vitrain.
	Coarse:	Through 10 mesh on 60 mesh.		
Coke		76·58	62·65	63·60
Carbon		3·01	0·71	0·65
Coke + Carbon		79·59	63·36	64·25
Tar		9·97	11·99	12·91
Gas (N.T.P.)		212 c.c.	238 c.c.	243 c.c.
	Medium:	Through 30 mesh on 90 mesh.		
Coke		72·88	62·33	63·96
Carbon		2·40	0·69	0·77
Coke + Carbon		75·28	63·02	64·73
Tar		11·55	13·12	14·64
Gas (N.T.P.)		221 c.c.	250 c.c.	257 c.c.
	Fine:	Through 200 mesh.		
Coke	—	—	—	—
Carbon	—	—	—	—
Coke + Carbon	83·66	70·23	64·73	66·18
Tar	4·15	8·26	12·45	15·12
Gas (N.T.P.)	222 c.c.	209 c.c.	237 c.c.	226 c.c.

Analytical Data.—The carbonising results are recorded in tables I and II. As indicated above, the numbers for the "fine" specimens are practically valueless, on account of the loss or removal of uncarbonised coal from the hot zone. Whilst the gas and coke values are appreciably reduced, the loss of tar is partly compensated in some cases by the chloroform extract from the uncoked coal.

FIG I.

TEMPERATURE OF CARBONISATION 600°.



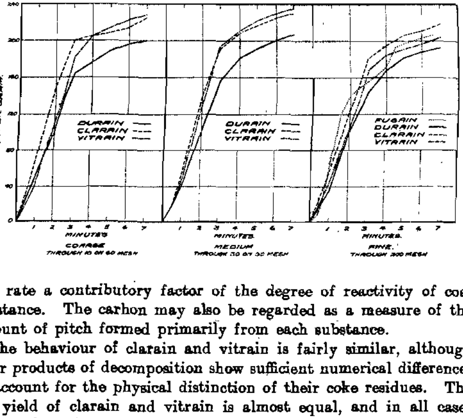
In considering the results from the "coarse" and "medium" specimens, it is to be seen that durain yields a much higher coke residue than clarain and vitrain, whilst the latter somewhat unexpectedly produces invariably a little more coke than the former.

An interesting feature is the amount of free carbon formed. At 900° this is considerably higher with durain than with clarain and vitrain, showing that the primary liquid products are more

susceptible to secondary decomposition or "cracking" at that temperature. On the other hand, at 600° no carbon whatever is produced from durain, whilst the amounts from clarain and vitrain are only slightly reduced (except in one case). This seems to indicate a considerable difference in the chemical nature of the primary decomposition products of durain on one side and of clarain and vitrain on the other. This observation is quite in accordance with Tideswell and Wheeler's assumption of varying proportions of "reactive" and "inert" groups in the different coal constituents. However, it is suggested that the very considerable discrepancies in the amount and composition of mineral ingredients (to be described in the succeeding paper) influences catalytically the course of primary and secondary decomposition, and may be at

FIG 2

TEMPERATURE OF CARBONISATION 900°.



any rate a contributory factor of the degree of reactivity of coal substance. The carhon may also be regarded as a measure of the amount of pitch formed primarily from each substance.

The behaviour of clarain and vitrain is fairly similar, although their products of decomposition show sufficient numerical differences to account for the physical distinction of their coke residues. The gas yield of clarain and vitrain is almost equal, and in all cases larger, than that of durain. The differences in gas yield at 900° are much *less pointed than those at 600°. This is due to the* secondary decomposition of heavy hydrocarbons and cracking of tar oils running back into the hot zone. All samples of gas contained hydrogen sulphide and burned with a luminous flame, the order of luminosity being clarain, vitrain, durain, fusain.

EXPERIMENTAL.

The electric furnace employed for heating the retort tube has been somewhat modified from that originally described. It consists of two vertical silica tubes wound in series with nichrome wire of the same length and gauge on each tube. The furnace tubes are open at both ends, and by a height-adjusting attachment the coal charge may be placed in any desired portion of the heating tube. In all experiments here described, the retort was fixed with the coal charge in the middle of the heating tube, thus being in the hottest part of the tube. Care was taken to avoid the indraught of cold air into the furnace tube by placing asbestos collars at each end. In the second heating tube was placed a calibrated platinum-platinum–iridium thermocouple with the junction in a position corresponding with the centre of the coal charge in the other tube. Before making a test, the furnace was heated until a constant temperature was attained. The constancy of temperature in both tubes was frequently checked by transferring the thermocouple from one tube to the other, when only negligible differences in temperature were detected.

After inserting the coal sample and silica piston in the retort tube, it was connected to the scrubber and eudiometer, the latter being filled with a mixture of glycerol and water. The air in the retort and scrubber was not removed, as only total volumes were read and no gas analyses were made. When ready, the retort was plunged into the furnace tube, when distillation quickly began. Readings of the volumes of gas generated were made at intervals of half a minute.

At the end of the distillation period, the retort tube was removed from the furnace, but left connected to the eudiometer until the gas had attained the ordinary temperature. The final measurement of the gas was then made, the eudiometer disconnected, and the scrubber and retort tube containing the coke were extracted with chloroform for the removal of tar. The chloroform extract was evaporated and dried, and the residue weighed; the coke was also weighed after drying. Small quantities of retort carbon produced by the decomposition of tar vapours on the hot retort walls were weighed separately.

The temperatures selected for treating the specimens were 600° and 900°. The former is the maximum temperature which Tideswell and Wheeler employed in their experiments. The latter was chosen as likely to produce greater changes in the solid coking residues and as more nearly approximating the temperatures customarily employed in industrial carbonising methods. The

three sets of specimens differing in size of particles only of durain, clarain, and vitrain, and fusain of original size, were submitted to tests at both temperatures in a strictly comparative fashion.

At 900°, a heating period of exactly seven minutes was employed, beyond which the evolution of gas became very slow. It should be stated that in experiments extended for longer periods it never ceased entirely, which is to be explained by the fact that under the conditions of working, part of the liquid products was able to run back into the hot zone of the retort, where they are again and again subjected to gasification by secondary thermal decomposition or "cracking." The volume of gas thus generated is fairly constant.

In the tests at 600°, it was found necessary to prolong heating to fifteen minutes, after which the gas-production curves become practically straight horizontal lines.

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XXXI.—*The Mineral Constituents of Banded Bituminous Coal. Studies in the Composition of Coal.*

By RUDOLF LESSING.

THE peculiar behaviour on carbonisation of fusain, durain, clarain, and vitrain described in the preceding paper made it appear possible that the differences observed were not entirely due to the composition of their organic constituents, but that they were at any rate influenced or accentuated by the catalytic effect of their mineral components. The influence of catalysts on the spontaneous combustion and particularly on the carbonisation of coal was discussed at length in the William Young Memorial Lecture of 1914 (Lessing, "Catalysis in the Gas Industry," *Trans. North Brit. Ass. of Gas Managers*, 1914, 65; *J. Gas Lighting*, 1914, **77**, 570), and a good deal of evidence goes to show that the "ash" contents of coal play an important rôle in its thermal decomposition. By inference it may be assumed that the mineral contents of decaying vegetable matter, and adventitious inorganic material in contact therewith, have likewise exerted an influence on the formation of coal or its constituents. Experiments in connexion with an investigation of the coal-washing process, hitherto unpublished, have shown that the frac-

tions separable from coal slack by washing differ vastly, not only in the amount, but in the nature of the mineral matter which they contain. It seemed, therefore, interesting and promising to study the ash contents of fusain, durain, clarain, and vitrain, particularly as casual tests had shown that they differed considerably in appearance. For the purpose of this work Dr. Wheeler kindly supplied further large samples of the three substances which were required to make quantitative analyses possible. Durain and clarain were in pieces up to 30 mm. cube, vitrain in pieces of 5—10 mm. cube. Fusain was extracted from a large sample of the original coal which, like that used in the preceding research, came from the Thick Coal seam, Hamstead Colliery.

Percentage of Ash.—In view of discrepancies between the preliminary tests and some of Tideswell and Wheeler's ash figures (particularly for fusain and durain), and the probability that the inorganic constituents were not evenly distributed throughout the coal, the samples were not crushed and mixed as is usual in commercial analysis, but one or more individual pieces were ignited for each test. In table I the results obtained from the original samples (1 gram) and those of the bulk samples are given, together with the weight of sample used for individual tests.

TABLE I.

	Fusain.		Durain.		Clarain.		Vitrain.	
	Sample. Grams.	Ash. Per cent.	Sample. Grams.	Ash. Per cent.	Sample. Grams.	Ash. Per cent.	Sample. Grams.	Ash. Per cent.
"Fine" sample	1·0000	4·48	1·0000	4·94	1·0000	1·38	1·0000	1·16
"Coarse" sample			1·0000	7·22	1·0000	1·58	1·0000	1·16
Bulk sample. ...	5·9642	16·70	10·4024	5·68	11·4416	0·91	7·1680	1·07
	7·0522	14·66	12·1436	5·89	10·3068	1·13	11·2622	1·18
			11·9188	7·15	12·4234	1·49	11·1180	1·10
					12·5904	1·28	10·0082	0·98
					13·7908	1·17	10·0000	1·22
					13·2226	1·37		
					12·2544	1·22		
					13·3457	1·18		
	13·0164	15·59	34·4648	6·26	99·3757	1·22	49·5564	1·11

It will be noticed that the percentage of ash in clarain and vitrain is fairly constant, particularly when allowance is made for the enhanced experimental error in dealing with small percentages. The variation of the ash contents of durain is much more marked, although the percentage discrepancy to be calculated is not appreciably increased over that of clarain. Fusain, however, shows very considerable discrepancies between different samples. Apart from

the results from fusain given in table I, of which the "fine" sample was used in the preceding research and the bulk sample in the following analyses, amongst some picked samples, one was found containing as much as 28·75 per cent. of ash. The cause of these discrepancies is discussed below.

Appearance of Ash.—The ashes which were prepared by ignition of the samples in a muffle furnace on silica dishes at low temperature showed considerable difference in colour. The ash from fusain was dark brownish-grey, that from durain pure pale grey without the slightest brown tint, that from clarain a reddish-brown biscuit, and that from vitrain a pale biscuit colour. The large lumps were ignited uncrushed, and in the course of burning off produced lamina-

TABLE II.

Fusain.

	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO_2	Nil	0·78	8·06	8·84
Al_2O_3	0·19	8·33	4·06	8·66
Fe_2O_3				3·37
MnO				0·51
TiO_2				0·04
CaO	10·03	46·64	0·33	57·00
MgO	0·41	0·89	Nil	1·30
Na_2O	0·65	2·59	—	3·24
K_2O	0·14	0·53	—	0·67
SO_3	4·71	9·17	0·77	14·65
P_2O_5	—	—	—	—
CO_2	0·53	2·45 (diff.)	—	2·98
Total	16·66	71·38	13·22	101·26
Total by direct weighing	16·57	71·38	12·05	100·00

Durain.

	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO_2	Trace	1·46	49·08	50·54
Al_2O_3	Trace	19·94	24·20	42·34
Fe_2O_3				1·36
MnO				Nil
TiO_2				0·44
CaO	1·47	1·65	0·37	3·69
MgO	Nil	Nil	Nil	Nil
Na_2O	Nil	Nil	Nil	Nil
K_2O	Nil	Nil	—	Nil
SO_3	2·10	0·98	0·15	3·23
P_2O_5	—	—	—	—
Total	3·57	24·23	73·80	101·60
Total by direct weighing	3·48	23·81	72·71	100·00

TABLE II (*continued*).

Clarain.

	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO_2	0·12	0·96	8·36	9·44
Al_2O_3	0·10	12·66	7·86	16·58
Fe_2O_3				3·31
MnO				0·23
TiO_2				0·50
CaO	10·50	1·94	0·54	12·98
MgO	9·20	1·32	Nil	10·52
Na_2O	13·76	1·95	—	15·71
K_2O	Nil	Nil	—	—
SO_3	31·73	0·45	—	32·18
P_2O_5	Nil	0·01	Nil	0·01
Total	*65·41*	*19·29*	*16·76*	*101·46*
Total by direct weighing	65·24	17·86	16·90	100·00

Vitrain.

	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO_2	Trace	0·76	5·32	6·08
Al_2O_3	3·11	13·44	2·40	15·49
Fe_2O_3				3·09
MnO				0·13
TiO_2				0·24
CaO	12·42	2·46	0·34	15·22
MgO	1·04	0·83	Nil	1·87
Na_2O	16·12	1·55	—	17·67
K_2O	0·20	Nil	—	0·20
SO_3	28·62	1·49	0·78	30·89
P_2O_5	—	—	—	Trace
CO_2	6·69	—	—	6·69
Total	*68·20*	*20·53*	*8·84*	*97·57*
Total by direct weighing	*69·52*	*20·46*	*10·02*	*100·00*

tion, which it is suggested occurs parallel to the bedding plane of the coal. Clarain ash invariably contained intrusions of grey plates, indicating the presence of durain (or possibly fusain particles, this yielding a similar but darker grey ash). Vitrain ash contained also occasionally grey laminæ and some red, ferruginous specks. These foreign particles were picked out and rejected for analysis.

Analysis of Ash.—In view of the limited supply and the small ash content of the specimens, the complete analysis of the ashes presented considerable difficulties, as each had to be carried out on 0·5 gram. In the case of durain and clarain analyses could be repeated, but this was not possible in the case of vitrain. However,

it was considered advisable to record the figures as obtained, as they typify in their main aspect the character of the mineral constituents of vitrain and distinguish it clearly from durain, whilst showing considerable similarity with clarain.

The ashes were first separated into fractions soluble in water, soluble in hydrochloric acid and insoluble in hydrochloric acid. The water-soluble and hydrochloric acid-insoluble fractions were weighed after evaporation and drying. The hydrochloric acid-soluble portions could not be weighed directly on account of the formation of chlorides of the alkalis and alkaline earths, and were determined by difference. Each of the fractions was analysed separately, but the ammonia precipitates (oxides) of all three had to be combined.

The results are recorded in table II, and show very considerable differences between the four ashes. This is apparent both from the actual composition and the ratios of portions soluble and insoluble in water and acid.

Fusain.—The most striking feature of fusain ash is its high percentage of lime, amounting to 57·00 per cent. This is responsible for the high amount of soluble matter in this ash. Much of this lime is present as calcium oxide, and the ratio of the amount soluble in water and in acid is probably variable according to the amount of water used for extraction. The aqueous solution attracts carbon dioxide from the air, for which allowance has been made in the analysis. The actual free alkalinity corresponds with 6·7 per cent. of calcium oxide, the balance of which is present as calcium sulphate. Some sulphur may have been introduced in these analyses from the gas used for ashing the samples and in heating the alkali fusion of the insoluble portion.

Durain.—Nearly three-quarters of durain ash is insoluble in water or acid. The water-soluble portion amounts only to 3·5 per cent., which consists of calcium sulphate. The bulk of this ash consists of an aluminium silicate of the approximate composition of clay substance. The complete absence of manganese, magnesia, and alkalis calls for comment. The water extract of durain ash has a neutral reaction.

Clarain.—The soluble portion of clarain ash is almost as high as that of vitrain ash. It differs, however, from the latter in its lower percentage of lime. It is the only ash containing considerable amounts of magnesia, which is worthy of note in view of the importance of magnesium as a vital constituent of chlorophyll. It is also fairly high in soda, but contains no trace of potash. Iron is present in a sufficient quantity to account for the biscuit colour. Clarain ash has an alkaline reaction, and its alkalinity corresponds with 5·41 per cent. of sodium carbonate.

Vitrain.—Vitrain ash is somewhat similar to clarain ash, but shows some distinct differences. It contains the lowest percentage of insoluble matter as well as the lowest amount of silica of all four ashes. A distinct difference from clarain is the low magnesia figure. Practically all the lime is present as sulphate; soda is high, and part of it is present as sulphate, another part as carbonate. The high percentage of water-soluble substances accounts for a tendency of some particles to melt at the temperature of ignition. The small amount of matter insoluble in acid is in accordance with the absence of débris from this ingredient observed by Stopes, and with its probable colloidal nature. The alkalinity of vitrain ash corresponds with 5·19 per cent. of sodium carbonate.

Discussion of Results.

The fact that different portions of one and the same lump of coal contain different amounts of mineral matter is obvious and well known to all who have to deal with the analysis of coal, ever since de Marsilly (*Compt. rend.*, 1848, **46**, 882) observed "that however pure a piece of coal may be, and however homogeneous it may appear to the eye, its different parts do not yield the same proportions of fixed residue on incineration." Many thousands of analyses of the ash of different portions of a coal-seam must have been made from time to time for commercial purposes, the results of which have not been published. There are, however, on record comparatively few analyses of the ash of clearly defined constituents of coal, such as the composition of the ash of "mineral charcoal" (fusain) from Better Bed and Haigh Moor reported by Thorpe ("Coal, its History and Uses," 1878).

The separation by Stopes of four distinct ingredients from bituminous coal made it possible to inquire more closely into their mineral constituents. Kendall pointed out (*Rep. Brit. Assoc.*, Newcastle, 1916, 395) that there are three sources of mineral matter in coal, the mode of distribution of which is of great economic consequence, some being separable and others not, namely: (1) The residue of the mineral constituents of the plants composing the coal; (2) detrital matter blown or washed into the deposit; (3) the calcite, iron pyrites, etc., segregated as veins in the seams.

In amplification of this statement Stopes and Wheeler ("Monograph on the Constituents of Coal," 1918) discuss the probability that part of the inherent ash in plants may be lost in the process of coal formation, a fact which renders the problem of identification of individual coal constituents still more complex.

In view of the small amounts of material handled in this research,

and the complex analytical procedure followed, it is somewhat speculative to form definite conclusions as to the relation which the elements in these ashes have to each other, and still more so as to the combination in which they occur in the original coal before incineration.

It seems quite inadmissible to go yet further and postulate on the relationship of the ashes to the mineral constituents in the plants from which the coal has been formed. Any suggestions of a theoretical nature in this state of ignorance must, therefore, be regarded as tentative and require further proof by the analysis of ashes from a great variety of coals and their components, instead of relying on the present results obtained from one particular coal.

Moreover, the ashes, even after "hand picking" of particles obviously belonging to one of the other groups, were by no means homogeneous mixtures, but specks of white and reddish-brown substances could be easily discerned in the biscuit coloured or grey bulk. They no doubt represent the ash of individual plant fragments or mineral intrusions (lime, pyrites) in the coal substance.

The results are, however, considered definite enough to indicate the following suggestions:

Fusain.—The large proportion of lime and soluble matter makes it highly probable that the bulk of this ash is due to infiltration of lime salts, most likely in the form of calcium hydrogen carbonate, and that this is present in the fusain as calcium carbonate, more or less evenly distributed throughout the porous substance of this "mineral charcoal." Such infiltration would explain the discrepancy of ash percentage observed in various samples of fusain. The infiltration theory finds support by some experiments on the direct extraction with hydrochloric acid of fusain before incineration. Three samples were used, one of them being identical with the "fine" sample of table I, another being similar to the bulk sample, and a third consisting of a lump of fusain about 20 mm. long by 10 mm. thick. On warming these samples with the acid, a copious liberation of carbon dioxide took place. The following percentage figures were obtained:

	(1.)	(2.)	(3.)
Total ash	4·48	13·30	28·75
Extracted by hydrochloric acid from coal	19·96	47·07	40·70 of ash.
Extracted by hydrochloric acid from remaining ash	13·08	20·83	14·09 ,,
Insoluble	66·96	32·10	45·21 ,,

The differences in solubility are no doubt due to the presence of varying proportions of pyrites which may or may not be similarly caused by infiltration.

The presence of large amounts of calcium carbonate in fusain suggests comparison with the composition of the petrifactions known as "Coal Balls" (Stopes and Watson, *Phil. Trans.*, 1908, [*B*], **200**, 167). These, however, always contain about 10 per cent. of magnesia, whilst this is present to a small extent only in fusain ash. It is also worthy of note that the thin veins of white mineral found along the cleavage planes contain from 40 to 45 per cent. of calcium carbonate. This further supports the view that infiltration of calcium salts has taken place at one period of the formation of the coal seam through cracks or between the stratified layers and into the very porous structure of the fusain particles.

Durain.—The composition of durain is comparatively simple, since many of the minor constituents are entirely absent and others only small in quantity. It consists to the extent of 93 per cent. of alumina and silica. The presence of a large percentage of alumina in the ash from plants or plant products suggests at once the presence of, or origin from, lycopods, which are characterised by a high aluminium content. This important property of lycopodia was shown by Aderholt (*Annalen*, 1852, **82**, 111), Ritthausen (*J. pr. Chem.*, 1853, **58**, 134), Church (*Chem. News*, 1874, **30**, 137), and more recently by a comparative study of many other species by Kratzmann (*Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 311).

Since the lycopods are regarded as largely forming the bulk of the coal measures, the high alumina percentage in durain would be in accordance with palæobotanical and other evidence.

However, the absence of alkalis, magnesia, and the low lime figure call for caution. Moreover, it so happens that the ratio of alumina and silica is practically identical with that obtaining in "clay substance" (kaolinite, $Al_2O_3,2SiO_2,2H_2O$). The colour of fusain ash is a pure grey and almost white, thus proving the freedom from the colour-giving constituents which one would expect in the ash from plant fragments, but their absence may be due to their removal from the original plant substance during the course of coal formation. It was, therefore, considered useful to compare the ratio $Al_2O_3 : SiO_2$ in lycopodia amongst themselves and with that obtaining in coal constituents and "clay substance." The values on p. 264 were obtained.

Whilst one might suspect that the mineral constituents in present-day plants differ from those grown in a palæozoic climate and habitat, this $Al_2O_3 : SiO_2$ ratio indicates that the fusain and durain are in an entirely different class from the clarain and vitrain. The latter gave a ratio which is quite comparable with that of the ash of lycopodia, but the ratio in the former differs very considerably. It is so close to the ratio in "clay substance" that one is forced to

	Percentage in ash.		
	Al_2O_3.	SiO_2.	$\frac{Al_2O_3}{SiO_2}$.
L. chamaecypar, with spores (Aderholt) ...	51·85	13·60	3·81
,, without spores (Aderholt)	57·36	12·96	4·43
L. clavatum (Aderholt)	26·65	13·94	1·91
,, (Ritthausen)	39·07	18·82	2·11
,, ,, ...	22·20	13·01	1·71
,, (Church)	15·24	6·40	2·38
L. complanatum (Ritthausen)	37·87	10·06	3·76
L. alpinum (Church)	33·50	10·24	3·27
L. selago (Church)	7·29	2·53	2·88
Average ratio			2·92
"Mineral charcoal"—			
"Better Bed" (Thorpe)	33·8	38·7	0·87
"Haigh Moor" (Thorpe)	28·7	36·1	0·80
Fusain (Lessing)	8·66	8·84	0·98
Durain ,, ...	42·34	50·54	0·84
Clarain ,, ...	16·58	9·44	1·76
Vitrain ,, ...	15·49	6·08	2·55
Kaolinite (calcined) (Theory)	45·87	54·13	0·85

assume the presence of clay or a silicate of the same composition in durain and fusain. Whether this silicate was deposited in the plant or was produced like clay from rocks during the formation of the coal is impossible to say. The observation by Stopes that the mass of plant fragments in durain consists of spores embedded in a matrix of granular material makes it not impossible that the silica may be derived from earthy matter with which the spores originally became contaminated.

Clarain and Vitrain.—The composition of the ashes of these two substances make it very probable that they represent mainly the remainder of the original plant ashes. Both contain considerable quantities of alkali, are high in sulphur (which is largely due to the retention of organic sulphur by the alkali), and have a fairly uniform percentage of total ash. The alumina in both suggests their derivation from lycopodia, and, as appears from the above, the Al_2O_3 : SiO_2 ratio agrees quite well with that found in some of the existing species. Moreover, the bulk of the alumina in clarain and even more so in vitrain is soluble in acid in contradistinction from the alumina in durain, of which the greater portion is insoluble in acid.

The two ashes are very similar save in one respect, namely, the magnesia content. Clarain contains as much as 10·52 per cent. of magnesia, as against 1·87 per cent. in vitrain and a similar amount in fusain. Whilst no direct inference can be drawn from this fact, the magnesia suggests the presence of degradation products of leaf substance containing chlorophyll in clarain. Stopes (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 480) found that "the clarain is the portion

most interesting to the palæobotanist, for in it lies the greatest variety of recognisable plant tissues and structures. There may be in it clear bands and zones showing each disintegrated plant substance, also bands of clear cuticle, spore exines, resin bodies, and other structures, and among this variety of material plant stem tissues, leaf-tissues and so on may be preserved and may even fill the whole area of sections."

The proved presence of leaf-tissues in clarain and of magnesia in its ash may be a mere coincidence. Indeed, it is somewhat difficult to account for the quantities found. According to Willstätter, green leaves contain on an average 0·8 per cent. of chlorophyll, which in its turn yields 4·5 per cent. of pure magnesia on incineration. The magnesia may rise to 8 per cent. in ætiophyllin. Even allowing for a considerable concentration of magnesia during the process of coal formation, these amounts are scarcely large enough to account for the percentage found without resorting to speculation on a higher chlorophyll and magnesia content in palæozoic plants or on an accumulation of magnesia from successive generations of leaves. It is, however, considered worth while to draw attention to this peculiar distinction of clarain from the other constituents.

Conclusion.

The results obtained from this research can only be considered as of a preliminary nature, and are recorded mainly in order to stimulate research in this direction, which can only be successful if a great variety of coals are investigated by "rational" analysis. Refining of coal by washing is still in a crude stage on account of lack of knowledge of the distribution of the ash. Evidence exists that differences in the amount and composition of inorganic constituents in coal can direct the course of its thermal and probably spontaneous decomposition. It is further likely that the course of formation of coal and its main constituents has been similarly influenced by plant débris and adventitious impurities. More detailed knowledge of the mineral constituents in coal is, therefore, required, both from the theoretical and technical point of view.

In conclusion, I wish to express my thanks to Dr. Marie C. Stopes and Dr. R. V. Wheeler, who laboriously prepared most of the samples for me, and who assisted the investigations with much suggestive criticism, and to Mr. A. H. Raine, who has carried out the experimental work for this and the preceding paper.

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XXXII.—l-*Hexylsuccinic Acid.*

By Henry Wren and Henry Burns.

The interesting observations which had been made during the investigation of the racemisation of the optically active phenylsuccinic acids and their derivatives (Wren and Williams, T., 1916, **109**, 572; Wren, T., 1918, **113**, 210) appeared to render it desirable to examine the behaviour of a similar compound in which the phenyl group was displaced by an alkyl radicle of approximately the same weight. This was more particularly the case since, although a general survey of the literature would lead to the conclusion that the presence of a phenyl group directly united to the asymmetric carbon atom of a racemisable compound renders the substance more prone to racemisation than does a similarly placed alkyl group, a precise comparison of the effect under similar conditions does not appear to have been made. For this purpose, hexylsuccinic acid was selected. Circumstances have combined, however, to prevent the work being carried to completion, and as its continuation must be postponed for some considerable time, it was considered desirable to give the present short account of the resolution of the racemic acid and of the properties of *l*-hexylsuccinic acid.

Experimental.

r-Hexylsuccinic acid (28 grams; prepared according to the directions of Higson and Thorpe, T., 1906, **89**, 1469) and quinine (52·1 grams) were dissolved by gentle warming in ethyl alcohol (560 c.c.). Tufts of small needles slowly separated from the solution at the ordinary temperature, which, when air-dried, weighed 44 grams. The salt was purified by repeated crystallisation from alcohol, 20 c.c. of the solvent being used for each gram of material. The course of the resolution was followed by determining the specific rotation of the acid recovered from the successive filtrates, the observations being made in ethyl-alcoholic solution. In this manner, the following values were found: +12·97°, +7·55°, −2·44°, −8·7°, −13·7°, −17·3°, −20·2°, −22·6°, and −23·6°. The crop which had separated from the final mother liquor weighed 6·8 grams, and, on decomposition with dilute sulphuric acid and extraction with ether, gave 2·4 grams of *l*-hexylsuccinic acid, which melted at 81—83° and had $[\alpha]_D$ −26·0° in alcohol. It was finally purified by crystallisation from water containing 10 per cent. of

alcohol until the specific rotation of successive crops remained constant.

l-*Hexylsuccinic acid* separates from water or very dilute alcohol as a granular powder; it is freely soluble in the hot solvent, sparingly so in the cold, the solutions, however, showing a very pronounced tendency to supersaturation. It melts at 82—83°, whilst the racemic acid melts at 87°:

0·1302 gave 0·2840 CO_2 and 0·1035 H_2O. C=59·5; H=8·8.
$C_{10}H_{18}O_4$ requires C=59·4; H=8·9 per cent.

The specific rotation was determined in the following solvents:

In ethyl-alcoholic solution:

$l=2$, $c=4{\cdot}0025$, $\alpha_D^{15\cdot8} - 2{\cdot}13°$, $[\alpha]_D^{15\cdot8} - 26{\cdot}6°$.

In acetone solution:

$l=2$, $c=1{\cdot}4875$, $\alpha_D - 0{\cdot}98°$, $[\alpha]_D - 32{\cdot}9°$.

In benzene solution:

$l=2$, $c=1{\cdot}8775$, $\alpha_D + 0{\cdot}02°$, $[\alpha]_D + 0{\cdot}5°$.

Attempts to resolve *r*-hexylsuccinic acid by brucine or morphine in aqueous or alcoholic solution, or by strychnine in ethyl-alcoholic solution, were unsuccessful.

Behaviour of the Active Hexylsuccinic Acids towards Alkali.

Separate portions of the pure *l*-acid were heated under reflux on the water-bath with aqueous and aqueous-alcoholic (containing 10 per cent. of water) sodium hydroxide solution (1·183*N*; 20 c.c.) during five hours. The recovered acids had $[\alpha]_D - 26{\cdot}42°$ and $-25{\cdot}5°$, respectively, in ethyl-alcoholic solution; racemisation, therefore, did not occur in aqueous, and to only a very slight extent in alcoholic, solution, the slightly more marked effect of the latter reagent being in accordance with the recent observations of McKenzie and Wren (T., 1919, **115**, 609) on the behaviour of *l*-mandelic acid under similar conditions.

d-Hexylsuccinic acid is markedly more stable under the combined influence of relatively high temperature and alkali hydroxide than is *d*-phenylsuccinic acid (Wren and Williams, *loc. cit.*). Thus, in an attempt to utilise some crude active acids, a specimen having $[\alpha]_D + 13{\cdot}0°$ was heated with an excess of sodium hydroxide solution during five hours at 160°; the recovered acid had $[\alpha]_D + 10{\cdot}43°$, showing that racemisation had occurred to a comparatively slight extent, whilst under similar conditions, but with only two hours' heating, *d*-phenylsuccinic acid was almost completely racemised.

The authors desire to express their thanks to the Research Fund Committee of the Royal Society for a grant which has defrayed part of the cost of the investigation.

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XXXIII.—*Surface Tension of Mixtures of Water and Alcohol.*

By James Brierley Firth.

A method was required for conveniently determining small changes in concentration of the binary mixture, alcohol and water.

It appeared that a determination of the drop-number–concentration curve would provide a suitable method for this purpose, and it was with this object that the following experiments were carried out.

The utilisation of the drop-number–concentration curve as a means of analysis has been used successfully by Donnan and Barker (*Proc. Roy. Soc.*, 1911, [*A*], **85**, 557) and Lewis (*Phil. Mag.*, 1908, [vi], **15**, 499) for determining changes in concentration of dilute solutions.

The theory of the drop-pipette is that for a given size of opening the surface tension is directly proportional to the weight of the drop, and hence it may be used for determining relative surface tensions of solutions of different concentrations.

If V = total volume of the liquid used,

n = total number of drops formed,

then the volume of each drop $= \frac{V}{n}$.

If ρ is the density of the liquid, then the weight of each drop $= \frac{V}{n}$.

σ, the surface tension, is proportional to the weight of the drop; therefore

$$\sigma = \kappa\frac{V\rho}{n}$$

Similarly for another liquid:

$$\sigma_1 = \kappa\frac{V\rho_1}{n_1},$$

therefore
$$\frac{\sigma}{\sigma_1} = \frac{n_1\rho}{n\rho_1},$$
or
$$\sigma = \frac{n_1}{n}\frac{\rho}{\rho_1}\sigma_1.$$

The principle assumes a static equilibrium, which is not correct, since the phenomenon is really dynamic, and in order to give an absolute measure of surface tension a small correction would be necessary (Guye and Perrot, *Arch. Sci. phys. nat.*, 1901, [iv], **11**, 225; 1903, [iv], **15**, 132; *J. Chim. physique*, 1917, **15**, 164). This correction in utilising the drop-number–concentration curve as a means of analysis is unnecessary.

The drop-number for a constant volume will vary with the speed of dropping, since it takes an appreciable time for the freshly formed surface to attain equilibrium. It is essential, therefore, that the drops should form slowly, and that the rate of formation should remain as constant as possible throughout the series.

Duclaux (*Ann. Chim. Phys.*, 1878, [v], **13**, 76) determined the surface tension of mixtures of alcohol and fatty acids with water by means of the drop-pipette, and showed that the surface-tension–concentration curve takes the form of a hyperbola, and the surface tension may be calculated from the equation:

$$\sigma = \kappa(e^x - 1),$$

where σ = surface tension, and x is the percentage concentration by weight.

Experimental.

The alcohol was dried over quicklime and distilled off, then dried with metallic calcium, and finally distilled, the first and last runnings being rejected.

The apparatus was similar to that used by Donnan and Barker (*loc. cit.*), the dropping tip being 3·5 mm. in diameter.

The experiments were carried out in an electrically-heated thermostat at 25°, and the rate of dropping was adjusted as near as possible to nine drops per minute.

The drop numbers of mixtures of alcohol and water were determined for mixtures containing from 2 to 96·5 per cent. of water by volume. The drop numbers are the same concentration agreed to 1 in 500 drops.

Results.

The following table gives the measurements of drop numbers and surface tension, the surface tension being calculated from the equation:

$$\sigma = \frac{n_1}{n}\frac{\rho}{\rho_1}\sigma_1.$$

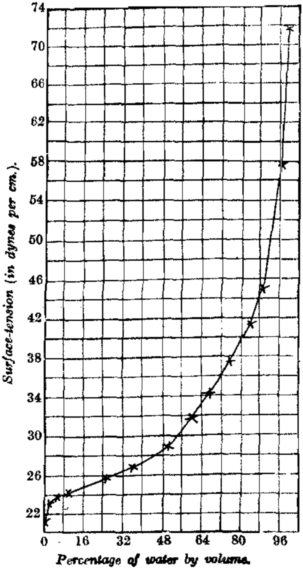
The surface tension for water at 25° was taken as 71·78 dynes per cm.

TABLE I.

Percentage concentration of water by volume.	Drop number.	Surface tension in dynes/cm.	Percentage concentration of water by volume.	Drop number.	Surface tension in dynes/cm.
0	1826	21·30	60	1480	31·88
2	1710	23·13	67·3	1395	34·24
5	1708	23·73	75	1285	37·50
10	1714	24·14	84	1170	41·30
25	1690	25·76	89·2	1090	44·91
36·5	1675	26·83	96·5	854	57·72
50	1613	28·74	100	690	71·78

The surface-tension–concentration curve is shown in the figure

The general results for binary mixtures have already been pub



lished by various authors (compare Worley, T., 1914, **105**, 260, 273), but as several important features have been revealed by the experiments it was thought desirable to record them.

There is a sudden fall in drop-number for 2 per cent. of water, then a further increase in the percentage of water up to 50 produces only a small change in drop-number; in fact, from 2 to 10 per cent. of water the drop-number is nearly constant. As the percentage of water increases beyond 50 the drop-number falls more rapidly with increased water content.

The results for the change in surface tension with concentration give a hyperbolic curve until a concentration of about 4 per cent. of water is reached, when the surface tension rapidly diminishes with diminution of water content.

It is interesting to note that the inflexion in the curve occurs at the point which practically corresponds with the concentration (4·4 per cent. of water) given by Young and Fortey (T., 1902, **81**, 717) for a mixture of minimum boiling point.

The utility of the drop-number–concentration curve as a means of analysis varies with the range over which analysis is required.

Where the water content is more than 50 per cent. the curve may be used to give a fairly accurate analysis, but for concentrations below this the change in drop-number with concentration is not sufficiently great to give trustworthy results, whereas with the apparatus employed differences in concentration between 2 and 10 per cent. of water could not be detected with any degree of certainty.

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XXXIV.—$\beta\beta'$-*Dichloroethyl Sulphide.*

By CHARLES STANLEY GIBSON and WILLIAM JACKSON POPE.

IN the late autumn of 1917 we were requested by the Chemical Warfare Department to study the preparation of $\beta\beta'$-dichloroethyl sulphide, $(CH_2Cl{\cdot}CH_2)_2S$, and in this connexion we thought it desirable to investigate carefully the interactions of ethylene and the two chlorides of sulphur. For obvious reasons, the results of this work remained unpublished, but as these reasons no longer exist, such of the information obtained as is of scientific interest

is now communicated. Since a number of workers in different countries were occupied with similar investigations, and their results, as reported, were often available for our information, we deal in the present paper only with our own work, and give the dates of the reports in which our results were communicated to the Government Department.

Interaction of Ethylene and Sulphur Dichloride.

The interaction of ethylene and sulphur dichloride was investigated by Guthrie some sixty years ago (*Quart. Journ. Chem. Soc.*, 1860, **12**, 116). He obtained a liquid product which possessed a vesicant action, and was doubtless a highly impure $\beta\beta'$-dichloroethyl sulphide; this observation was shortly afterwards confirmed by Niemann (*Annalen*, 1860, **116**, 288).

As the result of a number of preliminary experiments, we decided on the following as the most satisfactory method for preparing $\beta\beta'$-dichloroethyl sulphide by the direct addition of ethylene to sulphur dichloride, in accordance with the following equation:

$$2CH_2{:}CH_2 + SCl_2 = (CH_2Cl{\cdot}CH_2)_2S.$$

Sulphur dichloride (50 grams), of the correct composition, free from iron and showing the specific gravity of 1·6227 at 17°, is introduced into a set of glass bulbs which can be rapidly shaken by mechanical means; a small quantity (0·5 gram) of finely powdered, highly absorbent charcoal which has been well dried by heating in a current of hydrogen is suspended in the sulphur dichloride. Ethylene, prepared by the action of ethyl alcohol vapour on heated phosphoric acid, as described by Newth (T., 1901, **79**, 915), is freed from alcohol vapour by prolonged contact with water in a gasometer, and, after well drying by calcium chloride, is passed through the agitated sulphur dichloride, maintained at 40° to 45°, at such a rate that some escapes unabsorbed.

The ethylene is rapidly absorbed from the commencement, and the absorption ceases fairly suddenly when the reaction ends; owing to the volatility of sulphur dichloride, much of the latter is carried away by the excess of ethylene, and, in consequence, the quantity of ethylene absorbed is less than that indicated by the equation given above. The reaction proceeds similarly in the absence of charcoal, with the difference that absorption occurs much less rapidly in the latter stages and a smaller yield results. The temperature need not be rigidly limited; the reaction may be performed throughout at 50°, or may be started in the cold and allowed to warm up spontaneously or by externally applied heat to about 50°, but above this temperature unsatisfactory results are

obtained. Dilution of the sulphur dichloride with carbon tetrachloride has little effect on the yield or the purity of the product.

The liquid in the bulbs, which is of a straw-yellow colour, is now fractionally distilled under diminished pressure, and a fraction, boiling at 134—137°/50 mm., is collected; this crystallises on cooling and melts at from 5° to 9°. This product is about 50 per cent. by weight of the sulphur dichloride treated, and contains approximately 90 per cent. by weight of $\beta\beta'$-dichloroethyl sulphide. On oxidation with nitric acid, it gives *$\beta\beta'$-dichloroethyl sulphoxide*, described below.

The above method for preparing $\beta\beta'$-dichloroethyl sulphide was described in a report to the Chemical Warfare Department dated January 16th, 1918; it gives a better yield and is more expeditious than the method devised by V. Meyer (*Ber.*, 1886, **19**, 3260) and perfected by Clarke (T., 1912, **101**, 1583), which consists in converting (*a*) ethylene into ethylene chlorohydrin, (*b*) the latter into thiodiglycol by treatment with sodium sulphide, and (*c*) thiodiglycol into $\beta\beta'$-dichloroethyl sulphide by the action of hydrogen chloride. At the same time, the sulphur dichloride method is difficult to control, because $\beta\beta'$-dichloroethyl sulphide is acted on rapidly by sulphur dichloride; it is consequently necessary to work under such conditions that little or no sulphur dichloride remains long in contact with the $\beta\beta'$-dichloroethyl sulphide produced.

Interaction of Ethylene and Sulphur Monochloride.

On treating sulphur monochloride with ethylene at 100° and subjecting the liquid product to an elaborate method of purification, Guthrie (*Quart. Journ. Chem. Soc.*, 1861, **13**, 134) obtained a substance of slightly vesicant properties, to which he assigned the composition $C_4H_8Cl_2S_2$. Spring and Lecrenier (*Bull. Soc. chim.*, 1887, [ii], **48**, 629) showed that on oxidation with nitric acid this product yields β-chloroethylsulphonic acid, which is convertible into taurine, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$; the same β-chloroethylsulphonic acid was obtained by James (T., 1879, **35**, 806; 1885, **47**, 365) by the oxidation of β-chloroethyl thiocyanate. It is thus proved that Guthrie's compound is a disulphide of the constitution $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$. During the course of a recent discussion concerning the reaction between ethylene and sulphur monochloride (*J. Soc. Chem. Ind.*, 1919, **38**, 248T, 344R, 363R, 432R, and 469R), A. G. Green has contended that the interaction of ethylene and sulphur monochloride at 30° yields a product identical with that obtained by Guthrie at 100°, and suggests that this compound has the constitution $(CH_2Cl{\cdot}CH_2)_2S{:}S$, but this formula is

the less probable in view of the experimental evidence adduced by Spring, Lecrenier, and James. On treating sulphur monochloride with ethylene at a variety of temperatures between 70° and the ordinary temperature, we have ourselves never obtained Guthrie's compound.

An exploratory examination of the interaction of ethylene and sulphur monochloride showed us that $\beta\beta'$-dichloroethyl sulphide is formed at all temperatures between the ordinary room temperature and about 70°. The following method was adopted as the best and most expeditious for the laboratory preparation of $\beta\beta'$-dichloroethyl sulphide.

Sulphur monochloride was purified by repeated distillation with small additions of sulphur from glass vessels; in order to ensure the absence of the dichloride, 2·5 per cent. of sulphur was dissolved in the purified product, which then had a density of 1·6862 at 14·5° and boiled at 136·5—137·5°/760 mm. About 5 per cent. by weight of $\beta\beta'$-dichloroethyl sulphide is added to the sulphur monochloride, which is then heated to 55° in the absorption bulbs and vigorously agitated while a rapid stream of ethylene, well dried by calcium chloride, is passed through the liquid. During the passage of the ethylene, heat is evolved, and the temperature should be maintained at 60° by cooling and heating when necessary; absorption begins immediately, and very quickly attains a uniform rate, stopping almost abruptly when two molecular proportions of ethylene have been absorbed by each one of sulphur monochloride present. Towards the latter part of the reaction, the liquid becomes turbid, owing to separation of sulphur in a viscous form, and when reaction is complete it is convenient to heat to 100° to produce a homogeneous solution, which can be readily poured out from the bulbs. On cooling the straw-coloured liquid, a copious deposit of crystalline sulphur separates; the crystallisation is facilitated by seeding. After remaining for some time in the cold, an almost colourless liquid may be decanted fairly completely from the compact, crystalline sulphur; this liquid crystallises on cooling and melts at 9—11°. By distillation under diminished pressure, the liquid is found to consist of practically pure $\beta\beta'$-dichloroethyl sulphide containing about 3 per cent. of sulphur in solution. On distilling the hot liquid, before separation of the sulphur, under diminished pressure, $\beta\beta'$-dichloroethyl sulphide alone passes over, and, after sweeping residual vapour out of the distilling flask by a current of dry air, practically pure sulphur remains.

On cooling in ice-water, the distillate solidifies to a mass of colourless needles resembling glacial acetic acid in appearance, and melts, in general, at 12—12·5°; by repeated freezing, draining off

the residual liquid, melting, and again freezing, a product melting at 13—13·5° is obtained. This represents pure $\beta\beta'$-dichloroethyl sulphide, and was analysed, with the following results:

0·2616 gave 0·4725 AgCl. Cl=44·7.
0·2587 „ 0·3862 $BaSO_4$. S=20·5.
$C_4H_8Cl_2S$ requires Cl=44·6; S=20·2 per cent.

During the course of a large number of preparations, carried out in general accordance with the conditions described above at temperatures between 20° and 70°, on quantities of about 40 grams of sulphur monochloride, it was established that the yield of pure $\beta\beta'$-dichloroethyl sulphide varied between 90 and 98 per cent. of that theoretically possible from the sulphur chloride. The sulphur remaining after the distillation retained a mere trace of resinous matter, and no product other than $\beta\beta'$-dichloroethyl sulphide distils; it is therefore concluded that the reaction represented by the appended equation proceeds quantitatively:

$$2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2S + S.$$

It should be observed that the reaction between ethylene and sulphur monochloride is accelerated by rise of temperature, absorption being about three times as rapid at 60° as at 30°. Whilst no reaction other than that indicated by the above equation is appreciable up to 60°, absorption commences normally at higher temperatures, 80° to 85°, but the liquid soon darkens and hydrogen chloride is evolved; absorption then does not proceed to the normal extent, and a very impure product is obtained. If the product of interaction at 60° is not heated to 100° before separation of the sulphur, it is observed that the latter is deposited in a gummy condition on cooling, and that the crystallisation is incomplete. This retention of the sulphur in some kind of "pseudo-solution" becomes more marked as the temperature of interaction is lowered. The $\beta\beta'$-dichloroethyl sulphide added to the sulphur monochloride before the reaction is started exercises some kind of catalytic influence in hastening the absorption; in its absence, absorption commences very slowly, and only attains the normal rate gradually, whilst with this initial addition absorption sets in immediately and proceeds at an appreciably uniform rate until the reaction is complete. After cessation of the absorption, no trace of sulphur monochloride can be detected in the product.

The reaction between ethylene and sulphur monochloride at 60° proceeds normally in the presence of metallic lead, but if metallic iron or an iron salt is present, the liquid darkens and hydrogen chloride is evolved; it is thus of importance to use sulphur chloride which is free from iron in order to avoid the well-known chlorin-

ating action exercised by sulphur monochloride in the presence of iron salts.

The method for the preparation of $\beta\beta'$-dichloroethyl sulphide from sulphur monochloride described above was communicated to the Chemical Warfare Department in reports dated January 30th and February 14th, 1918. In accordance with an agreement concerning the mutual exchange of information between the Allied Powers, these, together with the earlier report of January 16th, 1918, were immediately communicated to France and America. The information thus rendered available, first, that Guthrie's reaction between ethylene and sulphur dichloride is capable of giving a satisfactory yield of $\beta\beta'$-dichloroethyl sulphide, and, secondly, that a previously unsuspected reaction occurs between ethylene and sulphur monochloride, and results in a theoretical yield of $\beta\beta'$-dichloroethyl sulphide, was first passed between the Allies in these reports. The whole of the output of this toxic material achieved in Britain, France, and America during the recent war resulted from the application to large-scale production of the two reactions first shown to be economically possible in these three reports.

At the request of Sir Richard Threlfall, certain of the energy constants of $\beta\beta'$-dichloroethyl sulphide were determined in this laboratory by Messrs. C. T. Heycock and W. H. Mills. These gentlemen determined the heat of combustion of the liquid substance in the calorimetric bomb as 743·3 Calories at constant volume; the heat of formation from rhombic sulphur, amorphous carbon, and gaseous hydrogen and chlorine is thus calculated as +67·9 Calories. Messrs. Heycock and Atkinson also determined the heat of formation of sulphur monochloride from rhombic sulphur and gaseous chlorine as $(2S,Cl_2) = +16{\cdot}35$ Calories, and, in view of the uncertainty attaching to the published values for the heat of formation of ethylene, Messrs. Heycock and Mills made a new determination, using ethylene which had been carefully purified by liquefaction and distillation, which gave the value $(2C,2H_2) = -6{\cdot}1$ Calories for amorphous carbon and gaseous hydrogen. From these data, the following thermal equation is derived:

$$2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2S + S + 63{\cdot}75 \text{ Calories.}$$

The heat evolution which accompanies the condensation of ethylene with sulphur monochloride is thus a very large one, and requires careful consideration in connexion with large-scale preparations.

$\beta\beta'$-Dichloroethyl sulphide has a density of 1·285 at 15°/4°; its refractive indices were determined by Mr. W. G. Palmer in this laboratory as 1·52776 for H_C, 1·53125 for Na_D, and 1·53999 for

H_F at 15°. The molecular depression of the freezing point by benzene was determined as 54·6; the latent heat of fusion is hence calculated as about 30 Calories.

Aluminium, lead, brass, iron, bronze, zinc, and tin are not acted on by $\beta\beta'$-dichloroethyl sulphide at the ordinary temperature; with the first three metals no appreciable action is noted at 100°, but the others named are attacked at this temperature, the action being most rapid in the case of tin. Titanic and stannic chlorides yield additive compounds with the substance. Sulphur dichloride acts vigorously on $\beta\beta'$-dichloroethyl sulphide at the ordinary temperature, but our preparations of sulphur monochloride do not attack the sulphide appreciably below about 70°; above this temperature, reaction occurs, with evolution of hydrogen chloride and formation of more highly chlorinated derivatives of ethyl sulphide.

On treating $\beta\beta'$-dichloroethyl sulphide with concentrated nitric acid and gently warming, it is converted into *$\beta\beta'$-dichloroethyl sulphoxide*, $(CH_2Cl{\cdot}CH_2)_2SO$; after diluting the solution and crystallising the precipitate from 50 per cent. alcohol, the sulphoxide is obtained in small, colourless plates melting at 110°:

0·2145 gave 0·3500 AgCl. Cl = 40·4.

$C_4H_8OCl_2S$ requires Cl = 40·5 per cent.

The behaviour towards oxidising agents furnishes a ready method for distinguishing between Guthrie's disulphide and the monosulphide.

On adding bromine (2 mols.) to an ice-cold solution of $\beta\beta'$-dichloroethyl sulphide (1 mol.) in chloroform, a deep orange-coloured precipitate quickly separates; this, although it rapidly loses bromine, is sufficiently stable to allow of filtration, desiccation, and analysis. Two analyses of the product thus obtained showed the presence of 64·3 and 63·5 per cent. of bromine, whilst the compositions $(CH_2Cl{\cdot}CH_2)_2S,2Br_2$ and $(CH_2Cl{\cdot}CH_2)_2S,Br_2$ require 66·8 and 50·2 per cent. of bromine respectively. On keeping the dried, orange-coloured substance, it becomes converted, with loss of bromine, into a bright yellow solid melting at 43—44°; this substance could not be further purified, owing to its instability, but was found to contain 48·5 per cent. of bromine and to yield the sulphoxide, $(CH_2Cl{\cdot}CH_2)_2SO$, melting at 110°, on treatment with dilute sodium hydroxide solution.

It is thus indicated that the yellow compound melting at 43—44° is the *dibromide* of $\beta\beta'$-dichloroethyl sulphide, corresponding with the sulphoxide, and that the orange-coloured substance is the *perbromide*.

Our thanks are due to Mr. G. M. Bennett, M.A., for valuable

assistance in connexion with the experimental work described in the present paper.

This paper is published with the concurrence of the Government Department concerned.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, February 2nd*, 1920.]

XXXV.—*The Action of Ethyl Chloroformate on Pyridine and Quinoline.*

By THOMAS HOPKINS.

COMPARATIVELY few experiments appear to have been carried out on the action of halogen derivatives of the simpler aliphatic esters or the somewhat closely related compounds, the acid chlorides, on pyridine and quinoline. The first investigations were those of Gerichten (*Ber.*, 1882, **15**, 1251) and Krüger (*Ber.*, 1890, **23**, 2608), who obtained pyridine-betaine hydrochloride by the interaction of chloroacetic acid and pyridine. It was found that at 202—205°, pyridine-betaine hydrochloride decomposes into pyridine, methyl chloride, and carbon dioxide. Below this temperature, however, pyridine-betaine appears to be quite stable. Rhoussopoulos (*Ber.*, 1882, **15**, 2006) treated quinoline with ethyl chloroacetate, and obtained the chloride of quinoline-betaine ethyl ester. Dennstedt and Zimmermann (*Ber.*, 1886, **19**, 75) studied the interaction of pyridine and acetyl chloride. They found that an additive product was first formed, and, on heating over the water-bath, the first products isolated were pyridine and dehydracetic acid. The latter is formed from the acetyl chloride, and the pyridine is regarded as acting by removing the elements of hydrogen chloride.

The final products of these reactions are colourless substances. With ethyl chloroformate, pyridine forms a colourless, additive *compound*, which rapidly changes to red. The additive compounds of pyridine with hydrogen chloride, methyl chloride, or benzyl chloride are all colourless substances. It does not appear possible to put forward any structural explanation of the intense colour of the compound formed from ethyl chloroformate and pyridine without recourse to the hypothesis of partial valency. As at present such an hypothesis does not admit of experimental verification, the cause of the colour has not been satisfactorily elucidated. The *compound* of quinoline and ethyl chloroformate is canary-yellow and is only stable at very low temperatures.

This reaction is interesting in two other respects. First, it furnishes a means for producing ethyl chloride, the ease of decomposition of the pyridine compound in the absence of moisture leading to the view that the pyridine may assume the rôle of a catalyst. Secondly, the interaction of pyridine and ethyl chloroformate may be utilised for detecting small quantities of pyridine in commercial ammonium nitrate. The pyridine is first extracted with about 30 c.c. of chloroform, and then one or two drops of ethyl chloroformate are added. The presence of pyridine is indicated by the appearance of a red tint.

EXPERIMENTAL.

Ethyl Chloroformate and Pyridine.

In a preliminary experiment, 79 grams of pyridine (1 mol.) and 108 grams of ethyl chloroformate (1 mol.) were used. The pyridine was placed in a round-bottomed flask, which was surrounded by a freezing mixture. The flask was attached to a reflux condenser, and the ethyl chloroformate added very slowly from a dropping funnel. The condenser was connected to two coiled receivers immersed in a freezing mixture, thence to a tube with lime-water, and finally to a tube containing bromine water. During the addition, a vigorous reaction took place, and the lime-water rapidly became milky, a strong stream of gas with a very sweet, ethereal odour issuing from the exit tube. When the addition of the ethyl chloroformate was complete, a dark red paste was formed in the flask. The contents of the latter were raised to boiling point, and a strong evolution of gas occurred during this process. The apparatus was then detached and the contents of the flask and the coiled receivers were examined. The liquid condensed in the coiled receivers was proved by analysis to be ethyl chloride. The contents of the flask consisted of a dark red oil and a black, viscous mass. The greater part of the oil distilled at 115—120°, and was pyridine. It contained also a white, amorphous solid, which distilled at about 230°. The same white substance was isolated from the black, viscous mass by solution in alcohol and crystallisation in a vacuum. It contained Cl = 28·89, whilst pyridine hydrochloride requires Cl = 30·73 per cent. The substance was soluble in water, and when the solution was rendered alkaline with sodium hydroxide and saturated with salt, pyridine separated. This experiment led to the conclusion that the products of decomposition of the reaction were ethyl chloride, carbon dioxide, pyridine, and pyridine hydrochloride.

In order to control the intensity of the reaction, xylene and ether were used as diluents, but in each case when either the ethyl chloro-

formate was added to the pyridine or vice versa, the reaction appeared to be equally vigorous. The same intense reaction was observed when the reagents were kept at $-10°$ during the addition.

The Influence of Moisture on the Reaction.—About 200 grams of pyridine distilling at 115—120° were twice fractionated over solid potassium hydroxide, and the portion distilling at 115° was collected separately and allowed to remain over sodium overnight. Gas bubbles were evolved, showing that moisture was present. Sodium wire was unsuitable, for it charred the pyridine completely.

The ethyl chloroformate was fractionated, and the portion distilling at 93° separately collected. Any free acid was first destroyed by adding a little calcium carbonate. This fraction was also allowed to remain over sodium for several days and re-distilled.

With these purified materials, the interaction between gram-molecular proportions of the two substances was studied in a desiccator containing sulphuric acid, which itself was kept cold by a freezing mixture. The pyridine was dissolved in 200 c.c. of dry ether contained in a wide-mouthed bottle. Through the opening in the lid of the desiccator a dropping funnel was fixed, the stem of which was drawn out into a capillary tube terminating about 2 cm. above the surface of the liquid in the bottle. The ethyl chloroformate was placed in the dropping funnel, which was then closed with a calcium chloride tube. To the side-tube of the desiccator two calcium chloride tubes in series were fixed. After twenty-four hours, the tap of the side-tube was adjusted to admit such an amount of dried air as would allow the ethyl chloroformate to enter at the rate of a drop per second.

The same colour changes took place as in the preliminary experiments, and effervescence set in when the addition became too rapid. The dark red product was thoroughly washed six times with fresh quantities of dry ether and kept in a vacuum overnight. Next morning the surface layer was white, owing to the vacuum not having been maintained. The layer was removed, and the rest of the mass showed a uniform rose-red colour. The nature of this product was then examined.

(1) The percentage of chlorine in it was estimated by the Carius method. Some difficulty was experienced in this, because the product was so sensitive to traces of moisture. Owing to the ease with which the substance decomposes when exposed for a short time to the atmosphere, several estimations had to be carried out before satisfactory results were obtained. When the operation of weighing and transferring to the tube was done expeditiously, the percentage of chlorine was found to vary from 19·2 to 19·46, whilst $C_8H_{10}O_2NCl$ requires Cl = 18·93 per cent.

(2) The red substance when exposed to the atmosphere quickly effervesced, thus showing that decomposition was taking place. Water decomposed it rapidly with a strong evolution of carbon dioxide and ethyl chloride.

(3) *Hydrolytic Decomposition.*—The compound (19·3 grams) was placed in a small flask attached to a reflux condenser, and about 50 c.c. of water were added down the condenser tube, when a vigorous decomposition took place. When the evolution of gas had slackened, the contents of the flask were kept gently boiling for one hour. The aqueous solution was clear but slightly yellow, and had a strong odour of pyridine. The aqueous solution was then distilled, and two fractions were obtained, namely, an aqueous distillate up to 150°, and a white sublimate which appeared to distil at about 220°.

The aqueous distillate was strongly alkaline with a strong odour of pyridine, and the sulphuric acid–dichromate test showed conclusively the presence of alcohol.

The weight of white solid recovered was approximately 40 per cent. of the original weight taken. It was readily soluble in water or alcohol, giving colourless solutions, but insoluble in ether. It was recrystallised from water, dried in a vacuum for two days, and finally washed six times with dry ether. It melted at 120—122° and distilled unchanged at 220°. Analysis showed it to consist of pyridine hydrochloride (Found: Cl = 30·09. C_5H_5N,HCl requires Cl = 30·73 per cent.).

It is evident that the products of hydrolytic decomposition are free pyridine, alcohol, carbon dioxide, ethyl chloride, and pyridine hydrochloride to the extent of about 40 per cent. This change may therefore be expressed quantitatively by the equation:

$$3C_5H_5NCl\cdot CO_2Et + 2H_2O = C_5H_5N + 2C_5H_5N,HCl + EtCl + 3CO_2 + 2EtOH.$$

Ethyl Chloroformate and Quinoline.

Experiments were carried out on the interaction of quinoline (b. p. 134—140°) and ethyl chloroformate in a manner analogous to that described above. A yellow, amorphous solid was formed, which was far more stable than the corresponding pyridine compound. It could be submitted to the atmosphere for a considerable time without decomposition. On heating at 100°, it decomposed into quinoline, carbon dioxide, ethyl chloride, and quinoline hydrochloride, although this decomposition is slower than in the case of the pyridine compound. Water decomposes the quinoline compound in a like manner to the pyridine compound. The

chlorine content of the substance was determined by the Carius method, and the results varied from 14·25 to 14·95, whilst $C_{12}H_{12}O_2NCl$ requires Cl = 14·92 per cent. The variation in the results may be caused by the quality of the quinoline employed, which was isolated by fractionating the technical product. Pure quinoline distilling exactly at 239° was obtained, and the experiments were repeated. The ethyl chloroformate had been specially purified. It was found, however, that the pure quinoline did not react with ethyl chloroformate at the ordinary temperature, at zero, or at −10°. They interacted only at the temperature of solid carbon dioxide, and formed a canary-coloured product, as in the preliminary experiments. When the yellow compound is removed from the solid carbon dioxide and allowed to remain at the ordinary temperatnre, it quickly liquefies and decomposes. The decomposition is brisk, and carbon dioxide and ethyl chloride are evolved. The extent to which this decomposition takes place was then investigated. In a test-tube 10 cm. long provided with a side-tnbe and stopcock was placed 0·32 gram of quinoline. The tube was closed with an air-tight stopper carrying a short tube with a stopcock. This served the purpose of displacing the air with dry carbon dioxide at the initial stage and sweeping out any ethyl chloride into a Lunge nitrometer. The tube was placed in solid carbon dioxide in a Dewar vessel, and the equivalent of ethyl chloroformate added drop by drop. Particular care was taken to avoid access of moisture, and the tube and its contents were allowed to remain in the solid carbon dioxide for five hours. It was then connected with the nitrometer, the tube allowed to remain in the air, and the issuing ethyl chloride collected over 30 per cent. potassium hydroxide. By this experiment, 24·8 per cent. of the available ethyl chloride was accounted for (theoretical, 27·16 per cent.). The residue contained the hydrochloride, which explains the discrepancy. The reaction is very sensitive to moisture, and it was found that where no precautions were taken to eliminate moisture, 23·3 per cent. of hydrochloride is formed in the decomposition, and the available ethyl chloride is much lessened.

The author is indebted to the Research Committee of Messrs. Nobel's Explosives Co., Ltd., and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation. He is also indebted to Messrs. Nolan and Hepworth for friendly criticism of the experiments.

THE RESEARCH LABORATORIES,
STEVENSTON.
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XXXVI.—*The Action of Nitric Acid on Unsaturated Hydrocarbons. The Action of Nitric Acid on Acetylene.*

By Kennedy Joseph Previté Orton and Phyllis Violet McKie.

The action of nitric acid, in contrast to nitrogen peroxide, on unsaturated (non-aromatic) hydrocarbons has not yet been thoroughly examined. Such references as are found in the literature indicate that complete oxidation to oxalic acid or carbon dioxide usually occurs. Baschieri (*Atti R. Accad. Lincei*, 1901, [v], **9**, i, 391) and Testoni and Mascarelli (*ibid.*, 1902, [v], **10**, i, 442; *Gazzetta*, 1903, **33**, ii, 319), on examining the action of fuming nitric acid on acetylene, obtained, however, a mixture of complex substances, the constitution and even the composition of which were not with certainty elucidated. J. Schmidt (*Ber.*, 1901, **34**, 619), who prepared from stilbene and nitrogen dioxide a dinitrostilbene, suggested that this behaviour foreshadows the manner of reaction with acetylene.

We have examined the interaction of nitric acid and acetylene under varying conditions of concentration, of temperature, and in the presence of metallic salts, in the first instance to ascertain whether tetranitromethane or substances such as nitroform, which could be easily converted into tetranitromethane by nitration, were produced. This quest has been highly successful, and thus a source of tetranitromethane, which has a certain usefulness as a high explosive, from inexpensive materials has been obtained.

Acetylene is absorbed with very great ease by absolute nitric acid, or by mixtures of nitric acid and sulphuric acid. With dilution of the nitric acid, the rate of interaction, and hence the readiness of the absorption, decreases. Rise of temperature and the presence of the catalyst (mercury salt) cause an increase in the rate of the interaction and readiness of absorption. In these comparative statements of the readiness of absorption, it is to be understood that the method of bringing the gas and the liquid into contact is unchanged. Obviously intimate intermingling of a gas and a liquid will promote absorption and interaction, and may lead to as ready an absorption by a dilute acid at low temperature as is with less efficient mixing only found at more favourable temperatures and concentrations of the acid.

The reaction is accompanied by a small development of heat. On the scale of our experiments, the temperature was kept thereby at 5—8° above the laboratory temperature.

The products of the interaction of acetylene and nitric acid are various; and the nature and the proportion of these products is largely determined by the concentration of the acid, by the temperature, and by the presence of a catalyst or of sulphuric acid.

The Italian investigators (*loc. cit.*) isolated from the interaction of acetylene and nitric acid (D 1·52; the proportions are not stated) at low temperatures small quantities of different solid products, some neutral and some acid, which were frequently explosive. Nitroform was also found among the products.

Omitting the products of reduction of nitric acid, the reaction *yields nitroform and certain substances, which can be converted* into tetranitromethane, carbon dioxide (and a trace of carbon monoxide), and other substances—among them sometimes oxalic acid ("O.S." in the tables)—which cannot be converted into tetranitromethane; the latter may predominate in certain circumstances, such as high or low concentration of the nitric acid or low temperature. Of the antecedents of tetranitromethane, nitroform usually amounts to about 75—85 per cent., and the others to about 15 per cent. Of the metals which we have tried as catalysts, only mercury causes a marked increase of the proportion of nitroform, etc., and at the same time reduces to a very small proportion the by-products which do not yield tetranitromethane. In fact, the reaction is simplified, and the acetylene is quantitatively represented by nitroform, etc., and carbon dioxide. Table I summarises the results of experiments, which illustrate the effect of concentration of acid, temperature, presence of mercury nitrate, or of sulphuric acid.

Under "t.n.m." in the table is the quantity of tetranitromethane (as a percentage of the acetylene reacting) which can be obtained from the product by a treatment described later. This quantity is a convenient measure of the extent to which nitroform and the other antecedents are produced under given conditions. If 2 moles of tetranitromethane were formed from one of acetylene, "t.n.m." would amount to 1508 per cent. in a quantitative yield, or if 1 mole of acetylene yields one of tetranitromethane, which is far more probable, 754 per cent.

TABLE I.

A. Varying Concentration of Nitric Acid. Temperature, 15°.

Experiment.	Percentage of nitric acid.	C_2H_2 absorbed by 100 grams of nitric acid. Litres.	"t.n.m." as percentage of C_2H_2 absorbed.
1	100·0	1·610	75·5
2	97·5	1·510	163·0
3	95·0	1·296	238·0
4	90·0	1·097	160·0
5	85·0	0·546	158·0
6	70·0	1·043	37·4

B. Sulphuric Acid present. Temperature, 15°.

Experiment.	H_2SO_4/HNO_3.	C_2H_2 absorbed per 100 grams of nitric acid. Litres.	CO_2 evolved per 100 grams of nitric acid. Litres.	CO_2/C_2H_2 by volume.	"t.n.m." as percentage of C_2H_2 absorbed.	"O.S." as a percentage.
7	0·11/1	1·336	0·295	0·25/1	148·5	77·9
8	0·5 /1	1·41	0·137	0·09/1	0·0	95·6
9	0·5 /1	1·615	1·092	0·67/1	129·0	57·8
10	2·6 /1	1·774	0·17	0·1 /1	0·0	95·9

In Experiment 9, 0·33 per cent. of mercuric nitrate was present. In Experiments 6 and 10 the temperature was 30°.

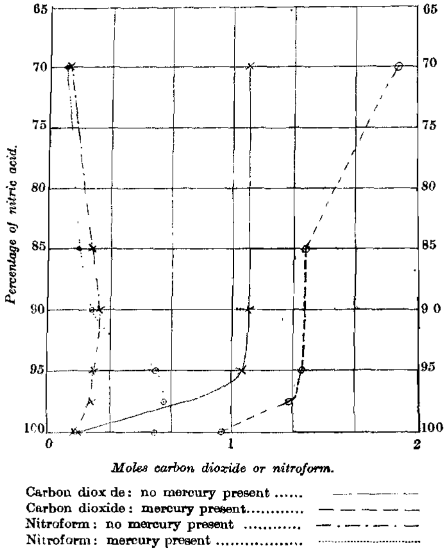
C. Mercuric Nitrate present, 0·66 per cent. Temperature, 15°.

Experiment.	T°.	Percentage of nitric acid.	C_2H_2 absorbed by 100 grams of nitric acid. Litres.	CO_2 evolved per 100 grams of nitric acid. Litres.	CO_2/C_2H_2 by volume.	"t.n.m." as percentage of C_2H_2.	"O.S." as a percentage.
11		90	1·490	2·27	1·52/1	204	9·82
D. Temperature Varied.							
12	−3°	95	1·20	0·54	0·394/1	104	61·0
13	15	95	1·296	1·04	0·8 /1	238	44·0
14	30	95	1·49	1·565	1·05/1	331	25·4
E. Mercuric Nitrate, 0·3—0·66 per cent. Temperature, 30°.							
15		95	1·571	2·22	1·41/1	523	0·0
16		100	3·456	4·87	1·4 /1	410	2·4
17		70	0·581	1·1	1·91/1	47	1·9

It will be seen that both a high concentration (in the absence of mercury salt) and a low concentration of nitric acid are unfavourable to the formation of nitroform and the other antecedents of

tetranitromethane. The optimum concentration is about 95—97 per cent. Obviously in the interaction of nitric acid and acetylene the acid becomes diluted, and the yield will only be a maximum when a small quantity of acetylene is absorbed by this acid (Expt. 15). To obtain the maximum quantity of nitroform (and tetranitromethane) in one operation the absorption of 3·5—3·7 litres of

FIG. 1.



acetylene by 100 grams of "100 per cent." nitric acid, to which 0·33 gram of mercury nitrate has been added, is best (Expt. 16). The yield of nitroform is then about 14·2 grams, and of tetranitromethane 16·7 grams (or 410 per cent.). At the lower concentrations (70 per cent.) of nitric acid, oxidation to carbon dioxide increases; the ratio $CO_2 : C_2H_2$ (by volume, molar) approaches, and in Expt. 17, under the influence of mercury nitrate, nearly

reaches 2 : 1. The dependence of the products of the reaction on the concentration of the nitric acid is well shown in Fig. 1. This indicates first the volume of carbon dioxide for one volume of acetylene, plotted against the concentration of nitric acid, (*a*) when *no mercury salt has been added*, (*b*) when mercury salt is present, and secondly the moles of nitroform for *one* mole of acetylene under similar different conditions; about 1 litre of acetylene has reacted with 100 grams of nitric acid.

Effect of the Presence of Various Metallic Salts.

The effect of the presence of small quantities of salts of platinum, silver, uranium, copper, and mercury on the reaction between nitric acid and acetylene has been examined. The metals were added as nitrates, except platinum, which was in the form of chloroplatinic acid. The quantities used were molar equivalents of the amount of the mercury nitrate required to form a 0·33 per cent. solution. In 95 per cent. nitric acid solution was complete, or nearly complete, except with platinum, when a heavy, yellow precipitate appeared and remained throughout. With copper a precipitate appeared during the reaction. Table II summarises the results. The nitric acid was diluted to 95 per cent., and the temperature was 30°.

TABLE II.

Experiment.	Metal.	C_2H_2 absorbed by 100 grams of nitric acid. Litres.	CO_2 evolved per 100 grams of nitric acid. Litres.	"t.n.m." as a percentage of C_2H_2.	Percentage of C in C_2H_2 becoming "t.n.m."	Percentage of C in C_2H_2 becoming CO_2.	Percentage of C in C_2H_2 becoming "O.S."
18 ……	Pt	2·68	2·25	203	13·5	41·8	44·7
19 ……	Ag	2·73	2·20	221	14·7	49·3	36·0
20 ……	Ur	2·60	3·32	222	14·9	63·6	21·5
21 ……	Cu	2·55	2·64	371	24·2	51·5	24·3
22 ……	Hg	3·02	4·38	453	29·18	70·81	0·0
23 ……	None	2·81	2·72	341	22·6	49·0	28·4

Mercury stands alone in having a markedly favourable effect on the rate of interaction, and hence on the readiness of absorption. Again, mercury is the only metal of those examined which exerts a beneficial influence on the production of nitroform and hence tetranitromethane. All the metals, save copper, favour oxidation of the acetylene, at the expense of the production of nitroform, etc.; uranium is peculiarly active in this respect. The experiment in which mercury is present stands out in that "other substances" are absent. Platinum has the opposite effect, and causes an increase in the proportion of by-products.

The proportion of mercury is important; the most favourable proportion lies below 1 per cent. Table III summaries the results of experiments made with the object of ascertaining exactly the best proportion, which is obviously 0·3—0·4 per cent.

TABLE III.

Temperature, 30°.

Experiment.	Percentage of nitric acid.	$Hg(NO_3)_2$ as percentage.	C_2H_2 absorbed by 100 grams of nitric acid. Litres.	CO_2 evolved per 100 grams of nitric acid. Litres.	"t.n.m." as a percentage of C_2H_2.	Percentage of C in C_2H_2 becoming "t.n.m."	Percentage of C in C_2H_2 becoming CO_2.	Percentage of C in C_2H_2 becoming "O.S."
24......	95·0	0·66	3·06	4·39	383	25·4	71·5	3·1
25......	95·0	0·33	3·02	4·38	453	29·2	70·8	0·0
26......	95·0	0·33	1·55	1·62	552	37·1	62·7	0·2
27......	97·5	0·28	3·16	4·34	429	28·5	68·2	3·3
28......	95·0	0·165	3·03	3·83	431	28·6	63·1	8·2
29......	95·0	0·0	2·81	2·72	341	22·6	49·0	28·4

The mercury salt appears to have more than one effect on the interaction of acetylene and nitric acid, and at different concentrations as well as at different temperatures one or other of these effects may be the more marked.

The most characteristic effect is the elimination of products other than the precursors of tetranitromethane or carbon dioxide. These products have been grouped together under "other substances," but two important groups can be distinguished. In the first place, when the nitric acid is highly concentrated, substances are produced in considerable quantity which do not on further treatment—"nitration"—yield tetranitromethane. These are probably the substances isolated by Mascarelli and his co-workers. Thus we find that with 100 per cent. nitric acid at 14° "O.S." may represent 86 per cent. of the acetylene absorbed, but in the presence of a mercury salt at 30° "O.S." is reduced to zero. The large increase in the yield of tetranitromethane from less than 100 per cent. in the first experiment to 460 per cent. in the second shows that the effect of a mercury salt is to cause the substitution of precursors of tetranitromethane for these other substances.

In less concentrated nitric acid, about 95 per cent., another effect becomes apparent. Now in the absence of mercury an important by-product is oxalic acid [$Ca(CO_2)_2,H_2O$ gave $CaCO_3=69·15$. Calc., $CaCO_3=68·50$ per cent.], which can be readily isolated from or estimated in the product. When 1·5 litres of acetylene are absorbed by 100 grams of nitric acid (95 per cent. at 30°), as much as 25 per cent. of the acetylene appears as oxalic acid. If a mercury salt is

present, however, only a very small quantity of oxalic acid is found, and there is a correspondingly large increase in the carbon dioxide. Direct experiment shows that a mercury salt does not cause the oxidation of oxalic acid by nitric acid, and it seems probable, therefore, that now, in the presence of mercury salt, some intermediary other than oxalic acid is directly oxidised to carbon dioxide.

The presence of a mercury salt also modifies the reaction of acetylene with a mixture of nitric acid and sulphuric acid. A comparison of experiments 8 and 9 (table I) demonstrates this effect. It will be seen that the precursors of tetranitromethane are only produced in the presence of a mercury salt, and, further, that concurrently there is more oxidation of the acetylene.

The mercury salt is without effect on the conversion of primary products of the interaction of acetylene and nitric acid into tetranitromethane, for addition after the absorption of the acetylene does not affect the yield of tetranitromethane in the subsequent treatment. The mercury salt then determines only the course of the primary interaction.

Formation of Nitroform and other Precursors of Tetranitromethane.—In order to account for the formation of tetranitromethane in the interaction of diacetylorthonitric acid, acetyl nitrate or nitric acid and acetic anhydride, Pictet and Genequand (*Ber.*, 1903, **36**, 2225) suggested that nitroform, which they isolated, or even trinitroacetic acid, precedes tetranitromethane. The formation of tetranitromethane by the nitration of nitroform had earlier been demonstrated by Schischkov (*Annalen*, 1861, **119**, 248), who used a mixture of nitric and sulphuric acids.

Nitroform, as its characteristic ammonium salt, can easily be isolated from the product. The estimation in the complex acid mixture is not so simple; but after removal of the "nitrous acid" by ammonium nitrate the nitroform can be distilled in a current of steam or extracted with ether, and then titrated in the distillate or extract with alkali hydroxide, or, better, with permanganate.

The quantity of nitroform thus determined does not represent more than 85—87 per cent. of the tetranitromethane which can be obtained from the product, and is in some circumstances less. No want of accuracy which can be detected in the method of estimation of the nitroform will account for this discrepancy between the quantities of nitroform and tetranitromethane.

Clear evidence that the product contains substances other than nitroform which yield tetranitromethane when heated with sulphuric acid is adduced by the following experiment. The product was obtained by passing acetylene into 95 per cent. nitric acid at

*30°, 0·33 per cent. of mercuric nitrate being present. The nitro*form found in a portion of the fresh product was equivalent to 15·6 grams of tetranitromethane, whereas the product yielded 20 grams. An equal portion of the product was heated at 85° for two hours before treatment with sulphuric acid. The yield of tetranitromethane in this portion was now 16·6 grams, and the nitroform therein was equivalent to 15·3 grams.

The yield of tetranitromethane also falls off, rapidly at first, if the product is kept for some time at the ordinary temperature, whereas the decomposition of nitroform in the product, which is also observed, is very much slower.

Obviously substances which can yield tetranitromethane have been destroyed by heating or keeping the product. It is clear that they have not been converted into nitroform, for the quantity of nitroform is approximately unchanged and, it is to be noted, after the heating, is nearly equivalent to the tetranitromethane.

The formation of nitroform from acetylene and nitric acid can be represented as the result of a simple addition:

$$CH⋮CH + 2HNO_3 \longrightarrow (NO_2)_2CH{\cdot}CH(OH)_2 \longrightarrow$$
$$(NO_2)_2CH{\cdot}CHO \longrightarrow (NO_2)_2CH{\cdot}CO_2H \text{ either} \longrightarrow$$
$$(NO_2)_2CH_2 + CO_2 \text{ or possibly } (NO_2)_2CH{\cdot}CO_2H + HNO_3 \longrightarrow$$
$$(NO_2)_3C{\cdot}CO_2H \longrightarrow (NO_2)_3CH + CO_2.$$

(The addition of nitrogen peroxide is not considered.)

Dinitromethane very readily reacts with nitrous acid (Duden, *Ber.*, 1893, **26**, 3003), yielding the *iso*nitroso-compound, which under the conditions would probably be oxidised to nitroform, thus:

$$(NO_2)_2CH_2 + HNO_2 \longrightarrow (NO_2)_2C⋮NOH \longrightarrow (NO_2)_3CH.$$

The *iso*nitroso-compound does not appear usually to be present in the product, for in normal experiments there is no marked indication of the blood-red colour which it yields with alkalis (Duden, *loc. cit.*). At lower dilutions of nitric acid, however, this reaction is obvious on rendering the product alkaline.

When nitroform is produced by the routes indicated above, one mole of acetylene yields one mole of nitroform and one mole of carbon dioxide; hence as a maximum only 50 per cent. of the carbon of the acetylene would become nitroform.

EXPERIMENTAL.

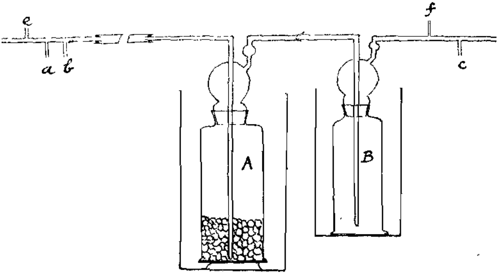
The essential parts of the apparatus are shown in Fig. 2. Acetylene is absorbed so readily, at least by sufficiently concentrated nitric acid at moderate temperatures, that the *Drechsel* bubbler (*A*), in which the end of the inlet tube is somewhat con-

stricted, serves as the reaction vessel; the bubbles of gas are broken by a layer of glass beads. This bubbler, which is nearly full, is immersed in a bath maintained at a constant temperature, usually 30°.

The second bubbler (*B*), which is placed in a cooling-bath, contains 30 c.c. of sulphuric acid (96—97 per cent.); all the oxides of nitrogen coming from (*A*) are absorbed in (*B*). No nitrous or nitric oxides have been found in the gas, which passes through the sulphuric acid. Safety devices for meeting a development of negative pressure or a sudden positive pressure are placed at *a*, *b*, and *c*. Samples of gas for analysis can be drawn off from the pipe line at *e* and *f*.

The acetylene, which was not purified, was dried by calcium

FIG. 2.



chloride. In this apparatus, good absorption (more than 90 per cent. under the best conditions) was obtained up to a speed of 400 c.c. per hour. Usually the speed was considerably less, about 150—200 c.c. per hour.

The nitric acid was prepared from a crude, fuming nitric acid (D^{15} 1·5), which contained much iodine as iodic acid, by distilling from an equal weight of sulphuric acid. The distillate had D^{15} 1·545; the acid contained 2·2 per cent. of "nitrous acid," as determined by potassium permanganate.

Mercuric nitrate (0·5 gram : 0·33 per cent.) is placed in the bubbler, then water (7·5 c.c. when a 95 per cent. nitric acid is used), and finally the nitric acid (138·6 grams = 90 c.c.). The mercuric nitrate dissolves completely; the quantity of 95 per cent. nitric acid just given will dissolve 1·2—1·3 grams at the ordinary

temperature. Absolute nitric acid dissolves very little mercuric nitrate which, at the beginning of the experiment, is in suspension, but dissolves later.

It is not advantageous to pass more than 4·5—4·6 litres of acetylene into *A*, although when absolute nitric acid is used this may be increased to 5 litres. As the reaction proceeds, the nitric acid is diluted; not only is the reaction then more tardy, and hence the absorption poorer, but oxidation of the acetylene, and hence the evolution of carbon dioxide, becomes more prominent. At the early stages of the reaction, very little gas leaves (*A*); later, oxides of nitrogen and carbon dioxide are evolved, towards the end of the experiment vigorously.

The results of typical experiments are summarised in table IV.

TABLE IV.

In all experiments, 0·33 per cent. of mercury nitrate was present.

Experiment.	Percentage of nitric acid.	C_2H_2 absorbed by 100 grams of nitric acid. Litres.	Nitroform. Grams.	CO_2 evolved by 100 grams of nitric acid. Litres.	"t.n.m." as a percentage of C_2H_2.	Percentage of C in C_2H_2 becoming "t.n.m."	Percentage of C in C_2H_2 becoming CO_2.	Percentage of C in C_2H_2 becoming "O.S."
30......	95·0	3·068	10·3	4·38	436	28·94	71·04	0·0
31......	97·5	3·163	10·5	4·34	430	28·8	68·5	2·3
32......	100·0	3·456	11·0	4·87	410	27·6	70·5	2·4
33......	100·0	2·883	9·9	4·07	448	29·73	70·3	0·0

Preparation of Nitroform.—The product is diluted 1 to 10, and then the nitrous acid removed by ammonium nitrate, 20 grams to 100 c.c. of the diluted product. The nitroform is then extracted by ether, preferably in a continuous apparatus. The ethereal extract is concentrated and added to alcoholic ammonia or alcoholic potassium hydroxide, when the salt crystallises out. From 100 grams of the product prepared under the best conditions, about 15 grams of the crude ammonium salt can be obtained.

Analysis of the Product; Nitroform, Nitrous and Nitric Acids.—The estimation of nitrous acid cannot be made directly on the product, for other substances which reduce permanganate are present. Two procedures have been followed. The permanganate titre of the product diluted 1 in 10 is determined; then either the nitrous acid is removed by aspiration or by boiling with ammonium nitrate (Gailhat, *J. Pharm. Chim.*, 1900, [vi], **12**, 9; Gerlinger, *Zeitsch. angew. Chem.*, 1902, **14**, 1250; they both use ammonium chloride). In the aspiration, it is not necessary to remove the whole of the nitrous acid, which is a very lengthy process. At a

given temperature and with a given air current, the percentage loss of nitrous acid from the solution follows the well-known law, and is independent of the initial concentration. At 16°, with the rate of air current 0·1 litre per minute, trials with known solutions of nitrous acid at various concentrations in aqueous nitric acid, and with known solutions of nitroform and nitrous acid in 7—8 per cent. nitric acid, show that 73·3 (72·8—73·9) per cent. of nitrous acid disappear in one hour. After the partial removal of the nitrous acid by aspiration or the complete removal by ammonium nitrate, the residual permanganate titre is determined, whence the "nitrous acid" can be calculated. Determinations of the nitrous acid made by these two methods agree fairly well, but the method of aspiration is probably the more trustworthy.

Determination of Nitroform.—Nitroform can be titrated in aqueous solution by alkali hydroxide in the presence of phenolphthalein (Hantzsch and Rinckenburger, *Ber.*, 1899, **32**, 631). We have devised a method, depending on the reduction of permanganate in the presence of sulphuric acid, which will be discussed more fully in another place. Recently, Erich Schmidt (*Ber.*, 1919, **52**, [*B*], 400) has described a procedure in which nitron is used as precipitant; this we have not yet tested, nor would it be easily applicable to our conditions, owing to the presence of nitric acid.

The product contains, besides nitrous acid and nitroform, other substances (for example, oxalic acid) which reduce permanganate. After removal of the nitrous acid, the nitroform may be extracted with ether and then titrated, or, preferably, distilled off and titrated with permanganate.

The following is a typical analysis: 2—5 c.c. of the "product" are added to 18—45 c.c. of $N/2$–N-alkali hydroxide; 5 c.c. are diluted with 10—15 c.c. of water, and 2—3 grams of ammonium nitrate added. The mixture is gently boiled for several minutes (five to ten), and then diluted to 100 c.c., acidified with 5—10 c.c. of 10 per cent. sulphuric acid, and distilled until the distillate is colourless (thirty minutes). The distillate may be collected in water or $N/10$-alkali; it is finally titrated with $N/10$-$KMnO_4$. One c.c. of $N/10$-$KMnO_4$ is equivalent to $151/80,000 = 0.0019$ gram of nitroform.

After destruction of nitrous acid and extraction of nitroform by ether, the residue still reduces permanganate. The reduction is but small under conditions most favourable for the preparation of nitroform or tetranitromethane. Some, and sometimes most, of the reduction of the permanganate by the residue is to be attributed to oxalic acid.

A rough estimate of the nitric acid in the product can be made

by deducting from the total alkali titre the alkali titre equivalent to the permanganate titre of the diluted product. As this deduction does not amount to more than 10 per cent. of the total alkali titre, a rough estimate of the nitric acid remaining is possible.

In a typical experiment, in which 4·27 litres of acetylene were absorbed by 138·6 grams of nitric acid (diluted to 95 per cent.), about 75 grams of nitric acid remained in the product, which weighed 123·5 grams. Deducting nitric acid, nitrous acid, and nitroform, the water in the product comes to 30 grams.

Analysis of Gases evolved during the Interaction of Acetylene and Nitric Acid.—The gas coming from the bubbler (*B*) is collected over a neutral, saturated calcium chloride solution in a large vessel of known capacity; the last part of the gas in an experiment is measured in a graduated vessel. Both carbon dioxide and acetylene are less readily soluble in saturated calcium chloride than in other saline solutions; at 14°, carbon dioxide has a solubility of 0·1 in 1, and acetylene 0·08 in 1, by volume.

The gas evolved during the heating of the product with sulphuric acid was collected in a similar manner. The liquid nearly filled the flask, which was ground on to a narrow condenser tube; this tube was carried on as a delivery tube for the evolved gas.

Table IV shows the large volumes of gas (carbon dioxide) collected. Nine-tenths, or rather more, are evolved during the interaction of acetylene and nitric acid when mercury is present, and the remainder during the heating with sulphuric acid. In the absence of mercury, 2/3—3/4 of the gas passes off at the first stage, and 1/4—1/3 at the second stage. These ratios strictly apply only to the carbon dioxide, which, however, largely predominates, especially in the first stage, less exactly to the total gas. The gas consists in the main of carbon dioxide with small percentages of acetylene and carbon monoxide, and traces of air. The gas given off in the heating contains much oxygen (up to 40—50 per cent.) from the interaction of nitric and sulphuric acids.

The gas was analysed in a "Bone and Wheeler" apparatus. The acetylene was absorbed by a 5 per cent. solution of potassium bromide saturated with bromine; the absorption is somewhat slow towards the end, but complete. After removal of the bromine vapour by the alkaline reagent, the carbon monoxide is absorbed by the ammoniacal cuprous chloride reagent. We have tested exhaustively this procedure on known mixtures of gases, and found it quite accurate. Usually, the gas of the first stage will contain: CO_2 = 75—80, C_2H_2 = 5—6, CO = at most 1 per cent.

Preparation of Tetranitromethane.—Originally, tetranitro-

methane was prepared by Schischkov (*loc. cit.*) from trinitroacetonitrile. Later, it was obtained in the exhaustive nitration of aromatic hydrocarbons (Will, *Ber.*, 1914, **47**, 704; Claessen, D.R.-P. 184229) by the action of diacetylorthonitric acid or acetyl nitrate on acetic anhydride (Pictet and Genequand, *loc. cit.*; Pictet and Khotinsky, *Compt. rend.*, 1907, **144**, 210), or from nitrogen pentoxide on acetic anhydride (Schenck, D.R.-P. 211198, 211199), or from nitric acid on acetic anhydride (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 224057; Berger, *Compt. rend.*, 1910, **151**, 813; Chattaway, T., 1910, **97**, 2099).

In preparing tetranitromethane from a hydrocarbon by exhaustive nitration, it is obvious that a low proportion of hydrogen to carbon, such as obtains in benzene, naphthalene, or acetylene, is desirable in order to economise nitric acid. Not only does the oxidation of a large proportion of hydrogen entail a corresponding loss of nitric acid, but the nitrating agent becomes diluted with water, and hence less efficient. On these grounds, benzene or its derivatives, or naphthalene derivatives, or acetylene are the most suitable substances. For various reasons, acetylene would be an excellent source of tetranitromethane. Whilst only some 4—5 per cent. of benzene nitrated can be converted into tetranitromethane, it has been shown in the foregoing that some 37 per cent. of the acetylene appears as this substance under suitable conditions.

The product from the interaction of acetylene and nitric acid contains very little tetranitromethane. If it is heated or first mixed with phosphoric oxide, sulphuric acid, or fuming sulphuric acid and then heated, tetranitromethane is formed.

A satisfactory procedure, in which all the nitroform is converted into tetranitromethane and the maximum yield is obtained, is to mix the product from 90 c.c. of 100 per cent. nitric acid with 190—380 grams of sulphuric acid or sulphuric acid containing 25 per cent. of sulphur trioxide. The sulphuric acid is added to the product, and care is taken that the temperature does not rise. The sulphuric acid from the bubbler (*B*), which contains a little nitroform, is also introduced. The mixture may be then directly distilled, but it is preferable to heat it, finally to 90—95°, under reflux until gas ceases to be evolved; this operation usually occupies about four hours. For reasons given in the foregoing, it is important that the product is mixed with sulphuric acid as soon as possible after the passage of the acetylene. That this mixture should then be kept for some time before heating or distilling is immaterial.

On cooling, much of the tetranitromethane will appear as an

oil, or even crystals; it may be collected by means of carbon tetrachloride or petroleum, but isolation by distillation is simplest.

The effect of certain variations in this procedure may be noted. The proportion of sulphuric acid may even be reduced below the limits given in the foregoing without producing any considerable diminution in the yield. Even if the proportion $H_2SO_4:HNO_3 =$ 0·75 : 1 by weight, the yield of tetranitromethane is only reduced by 10 per cent. The heating or the distillation of such a mixture is, however, attended with risk, as sudden decomposition, with evolution of gas, may ensue.

The addition of 20—25 grams of nitric acid to the mixture of the product and sulphuric acid before heating or distilling leads to an improvement of the yield (some 10 per cent.), especially if the conditions have otherwise been unfavourable; for example, if an excessive volume of acetylene has been passed into the nitric acid, or the temperature has been low, or the nitric acid too dilute. Under the conditions outlined in the foregoing, such addition of nitric acid has little, if any, effect.

As examples of the operation, the two following may be cited. The largest quantity of tetranitromethane (23·2 grams: 410 per cent. on the acetylene) in one operation was obtained by passing 5 litres into 138·6 grams (90 c.c.) of absolute nitric acid at 30° with 0·55 gram of mercuric nitrate in suspension. A better yield, of 453 per cent., was obtained by passing 4·6 litres into the same quantity of nitric acid diluted with water to 95 per cent. at the same temperature and with the same quantity of mercuric nitrate in solution; the weight of tetranitromethane isolated was 22·3 grams.

The Purification and Properties of Tetranitromethane.—The crude material, after washing with water, is nearly colourless, and melts at 13·4—13·5°. Thorough washing with dilute aqueous sodium carbonate does not change the melting point. After partial freezing and pouring off the remaining liquid three times, the substance melted at 13·75°, and the melting point was not raised by further fractionation. It has $D_{15·8}^{15·8}$ 1·65009.

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XXXVII.—*Synthetical Experiments with ββ′-Dichloroethyl Sulphide.*

By WILLIAM DAVIES.

A CONSIDERATION of the formula of penthiophencarboxylic acid (I)

$$S<\begin{matrix}CH{:}CH\\CH_2\cdot CH\end{matrix}>C\cdot CO_2H \qquad\qquad S<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H$$

(I.) (II.)

leads to the expectation that this acid would show properties analogous to those exhibited by benzoic acid. In order to test this hypothesis and with the object of synthesising penthiophencarboxylic acid, an attempt was made to condense ββ′-dichloroethyl sulphide with ethyl sodiomalonate, when it was expected that ethyl 1-thiopentamethylene-4:4-dicarboxylate would be produced, and that this ester, on hydrolysis and elimination of carbon dioxide, would yield 1-thiopentamethylene-4-carboxylic acid (II). This, on successive bromination and elimination of hydrogen bromide, should furnish the desired penthiophencarboxylic acid.

The condensation with ethyl malonate proceeded, however, in a different direction, as was evident from the fact that the product of the reaction, namely, ethyl γ-thiodiethylmalonate (which could not be obtained in a pure state), on hydrolysis and elimination of carbon dioxide, yielded γ-thiodibutyric acid,

$$S(CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)_2.$$

This acid was obtained in shining leaves melting at 97—98°, and for a dibasic acid is surprisingly sparingly soluble in cold water. It had already been described by Gabriel (*Ber.*, 1890, **23**, 2493), who prepared it (m. p. 99°) by hydrolysing the nitrile obtained by heating γ-chlorobutyronitrile with potassium sulphide.

Since the malonic ester condensation did not give the desired result, ββ′-dichloroethyl sulphide was condensed with ethyl sodioacetoacetate, and the condensation product submitted to alkaline hydrolysis. The acid isolated was again γ-thiodibutyric acid, showing that the condensation had resulted in the formation of ethyl αα′-diaceto-γ-thiodibutyrate, thus:

$$S<\begin{matrix}CH_2\cdot CH_2Cl\\CH_2\cdot CH_2Cl\end{matrix} + \begin{matrix}2CH_3\cdot CO\cdot CH_2\cdot CO_2Et\\+2NaOEt\end{matrix} \longrightarrow$$

$$S<\begin{matrix}CH_2\cdot CH_2\cdot CHAc\cdot CO_2Et\\CH_2\cdot CH_2\cdot CHAc\cdot CO_2Et\end{matrix}.$$

On alkaline hydrolysis this ester is decomposed in the usual manner to produce γ-thiodibutyric acid.

It is noteworthy that a much better yield of γ-thiodibutyric acid was obtained in the condensation with ethyl acetoacetate than in the corresponding experiment with ethyl malonate.

The conditions of experiment in the condensation with these two esters were varied (see pp. 302, 304), but in no case was there any evidence of ring-formation. The attempt to synthesise 1-thiopentamethylene-4-carboxylic acid had therefore to be abandoned.

Experiments were next made on the action of potassium cyanide on ββ'-dichloroethyl sulphide in the hope of obtaining ββ'-dicyanoethyl sulphide, $S(CH_2{\cdot}CH_2{\cdot}CN)_2$.

The *nitrile* obtained, however, was found to possess the abnormal formula $C_6H_{12}S_2(CN)_2$, and yielded on hydrolysis the *acid*, $C_6H_{12}S_2(CO_2H)_2$. It is possible that the nitrile has the composition $CN{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, but the matter has not been further investigated.

The next experiments were made with the object of preparing tetrahydrothiophen by the action of metals, especially sodium, on ββ'-dichloroethyl sulphide. Molecular sodium has, however, no action on the dichloro-derivative in boiling xylene, and when sodium is heated with it without diluent, there is no sign of reaction until the mixture is boiled, and then the sodium suddenly takes fire and forms sodium sulphide as well as sodium chloride. Boiling the dichloro-derivative with molecular silver and with finely divided copper also gave a negative result.

The action of ββ'-dichloroethyl sulphide on ammonia was then investigated, with the object of preparing 1:4-thiazan, thus:

$$S{<}{\begin{matrix}CH_2{\cdot}CH_2Cl\\CH_2{\cdot}CH_2Cl\end{matrix}} + NH_3 \longrightarrow S{<}{\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}}{>}NH.$$

Several alkylthiazans have already been prepared from ββ'-dichloroethyl sulphide by the action of amines (Clarke, T., 1912, **101**, 1583), but the parent substance has not been described.

ββ'-Dichloroethyl sulphide reacts only sluggishly with dry gaseous ammonia, even at 150°. On the other hand, when heated with excess of alcoholic ammonia under pressure at 60°, it is readily converted into 1:4-*thiazan*. Thiazan is a colourless liquid with a characteristic odour and boils at 169°/758 mm., or 5° higher than methylthiazan as recorded by Clark (*loc. cit.*). It has most of the properties common to organic bases, but the *platinichloride* has the formula $B,HCl,PtCl_4$, and the mode of formation of the *hydrochloride* (see p. 307) tends to show that the sulphur atom, as well as the imino-group can attach hydrogen chloride. Thiazan reacts

readily with potassium, and the *picrate* and *picrolonate* are characteristic, crystalline substances melting at 198° and 242° respectively. Thiazan combines with one molecule only of ethyl iodide, yielding a crystalline *ethiodide*.

The sulphone and sulphoxide corresponding with $\beta\beta'$-dichloroethyl sulphide (compare Spica, *Gazzetta*, 1919, **49**, ii, 299) are colourless, crystalline substances which do not possess the characteristic physiological properties of the parent sulphide, but the sulphone, especially in the form of fine dust, causes sneezing.

The $\beta\beta'$-dichloroethyl sulphide used in these experiments was kindly supplied by the Manager of the Avonmouth factory, where it was made by the sulphur monochloride process. It is noteworthy that it contained about 0·5 per cent. of diethylene disulphide, whilst the German "mustard gas," made by the thiodiglycol process, contained very much more.

EXPERIMENTAL.

Purification of $\beta\beta'$-Dichloroethyl Sulphide.

The crude substance is best purified by distillation in a vacuum, but the fraction of constant boiling point still contains a trace of diethylene disulphide. This can be practically completely removed by distillation under ordinary pressure, as the disulphide very readily sublimes at 190°, before the boiling point, 217°, of the dichloro-derivative has been reached. It is, however, more convenient to retain the small amount of impurity, and, after a reaction, to distil off the disulphide and unchanged dichloro-derivative in a current of steam.

The disulphide is very volatile, has a disagreeable odour, and melts at 111° (Found: C = 39·8; H = 6·8. $C_4H_8S_2$ requires C = 40·0; H = 6·7 per cent.). It was conclusively identified by a determination of the melting point when mixed with the diethylene disulphide (m. p. 111°), obtained by boiling alcoholic sodium sulphide with ethylene dichloride (compare Masson, T., 1886, **49**, 235).

Pure $\beta\beta'$-dichloroethyl sulphide boils at 120°/34 mm. and 122·5°/37 mm., and readily solidifies in cold weather, forming long, colourless needles, which melt at 13·5° to a liquid having a density of about 1·28 at the ordinary temperature. It is very sparingly soluble in water (compare Hopkins, *J. Pharm. Expt. Ther.*, 1919, **12**, 393), but can be readily hydrolysed by boiling alcoholic sodium hydroxide solution. This reagent and nitric acid are convenient substances with which to clean vessels that have contained $\beta\beta'$-dichloroethyl sulphide.

The sulphone is formed in almost theoretical amount by adding ββ′-dichloroethyl sulphide to excess of fuming nitric acid (D 1·50), the vigorous reaction being completed by cautiously boiling for a short time. On cooling, pouring into water, and keeping overnight, the sulphone is precipitated, and crystallises from alcohol in colourless, lustrous laminæ melting at 53·5°. An incautious smell of the crystals may cause violent sneezing. The sulphone is volatile in steam. As it is extremely difficult to detect the chlorine by the ordinary sodium test, it is better to reduce the sulphone by sodium in alcohol prior to testing (Found: C=25·3; H=4·2; S=16·9. $C_4H_8O_2Cl_2S$ requires C=25·1; H=4·2; S=16·75 per cent.).

The sulphoxide is formed quantitatively by gradually adding ββ′-dichloroethyl sulphide to excess of cold ordinary nitric acid and allowing the solution to remain for twenty-four hours at the ordinary temperature. The liquid is then rendered slightly alkaline by sodium carbonate, and the sulphoxide is precipitated. It separates from alcohol in colourless crystals melting at 109·5°. It dissolves readily in organic solvents, but is only sparingly soluble in water, which it renders faintly alkaline (Found: C=27·3; H=4·5. $C_4H_8OCl_2S$ requires C=27·4; H=4·6 per cent.).

Condensation of Ethyl Sodiomalonate with ββ′-Dichloroethyl Sulphide.

To a mixture of ββ′-dichloroethyl sulphide (25 c.c.: 1 mol.) and ethyl malonate (68 c.c.: 5 per cent. excess of 2 mols.) was slowly added a cold solution of sodium ethoxide prepared from 9·8 grams of sodium (5 per cent. excess of two atoms) in 150 c.c. of absolute alcohol. There was a slight evolution of heat, the liquid became cloudy, and with occasional shaking during half an hour the contents of the flask became almost solid through the deposition of sodium chloride. The product was allowed to remain overnight, the reaction completed by boiling for one hour on the water-bath, the alcohol distilled off, and the residual white mass treated with 150 c.c. of water and distilled in a current of steam. A little unchanged ethyl malonate passed over, together with a trace of diethylene disulphide.

There remained in the flask a heavy oil, which was extracted with ether. The ethereal solution was dried and evaporated, when the residual oil weighed 45 grams. This oil, which undoubtedly consisted largely of ethyl γ-thiodiethylmalonate, was a very pale yellow liquid with a not unpleasant odour somewhat reminiscent

of celery. As it decomposed on attempted distillation under diminished pressure, it could not be obtained in a pure state. Since its hydrolysis by aqueous or alcoholic alkali is liable to be very violent, aqueous alkali was at first employed, and the following procedure adopted.

The ester (15 grams) was poured into 100 c.c. of sodium hydroxide solution (47 per cent.), and the mixture shaken. The heat given out was sufficient to cause the liquid to boil gently, and this ebullition was maintained by the careful addition, with constant shaking, of a further 30 grams of the ester. The reaction having subsided, methyl alcohol (100 c.c.) was added, and the mixture boiled for two hours. After removing the ethyl and methyl alcohols by distillation, and cooling the gelatinous sodium salt which was formed, hydrochloric acid (200 c.c. of 30 per cent.) was added, and the thio-acid extracted six times with ether. The ethereal solution was dried and evaporated, leaving 17 grams of a brown syrup, which showed no tendency to solidify after scratching and keeping in a vacuum over sulphuric acid at 0° for a week. This crude acid was moderately soluble in water, and from it crystalline γ-thiodibutyric acid was obtained, in the following way. Carbon dioxide was eliminated by heating in an oil-bath for eight hours at 150—170°, when effervescence had completely ceased. The dark residual acid solidified on cooling, and a sample crystallised from ether melted at 40—60°. After boiling the ammonium salt of the acid with animal charcoal and repeatedly crystallising from water, the acid was obtained in colourless leaves with a nacreous lustre melting at 97—98° (Found: C=46·0; H=6·8. Equiv.= 102·7. $C_8H_{14}O_4S$ requires C=46·6; H=6·8 per cent. Equiv.= 103).

γ-Thiodibutyric acid is fairly readily soluble in hot water, very sparingly so in cold, but in order to obtain the acid in a crystalline condition, the aqueous solution employed must be dilute, otherwise, on cooling, the acid is precipitated as a brown oil. The acid is moderately soluble in alcohol, ether, or benzene, and crystallises from the last-named in microscopic plates on adding light petroleum. The acid does not distil in a current of steam or under diminished pressure. The ammonium salt slowly decomposes, with precipitation of the acid, when its aqueous solution is allowed to remain for several weeks.

Ethyl γ-Thiodibutyrate.

In order to ascertain whether the crude thiodibutyric acid contained any cyclic monobasic acid, the acid left after elimination of

carbon dioxide was esterified, and the ester fractionally distilled. The crude acid (41 grams), prepared from 100 c.c. of dichloroethyl sulphide and 272 c.c. of ethyl malonate, was esterified by boiling for three and a-half hours with 200 c.c. of absolute alcohol and 30 c.c. of concentrated sulphuric acid. The product was poured into water, extracted with ether, and the ethereal solution washed with sodium hydroxide solution and dried over calcium chloride.* On distilling the ester, the first fraction, apart from a trace of diethylene disulphide boiling at 107°/23 mm., consisted of 20 grams, which passed over at 180—200°/23 mm. On redistillation, 17 grams of this fraction were obtained at 188—197°/23 mm., mostly at 196°. The viscous, residual ester in the flask could not be distilled without decomposition, and has not been investigated.

Ethyl γ-thiodibutyrate is a colourless liquid with a disagreeable odour, insoluble in water, and readily miscible with organic solvents. It boils at 185°/11 mm. and 196°/23 mm., and has n_D^{20} 1·4701. On hydrolysis, γ-thiodibutyric acid (m. p. 97—98°) is formed:

0·0953 gave 0·1941 CO_2 and 0·0738 H_2O. C=55·6; H=8·6.
0·1387 „ 0·1224 $BaSO_4$. S=12·1.

$C_{12}H_{22}O_4S$ requires C=55·0; H=8·4; S=12·2 per cent.

Condensation of ββ′-Dichloroethyl Sulphide with Ethyl Sodiomalonate in the Absence of Alcohol.

In order to avoid any hydrolytic action of sodium ethoxide on the dichloro-derivative which may have taken place, even in the cold, the condensation was carried out in the following way. Ethyl malonate (136 c.c.) dried over calcium chloride was added to molecular sodium (20 grams) in boiling xylene. Dry benzene was added, and the mixture boiled gently on the water-bath. After four hours, all the sodium had disappeared, giving rise to the gelatinous ethyl sodiomalonate. ββ′-Dichloroethyl sulphide (50 c.c.) was slowly added with shaking, and the benzene solution boiled for ten hours. The benzene was then removed, water added, the mixture distilled in a current of steam, and the residual ester worked up as before. The yield of ethyl γ-thiodibutyrate was better

* In the first esterification the catalyst used was hydrogen chloride, and the resulting ester showed the physiological properties of "mustard gas," although there was not sufficient present to be separated by fractional distillation. This trace of ββ′-dichloroethyl sulphide was clearly formed by the action of hydrogen chloride on some thiodiglycol, doubtless obtained by the hydrolytic action of the slightly alkaline ethyl sodiomalonate on the dichloro-derivative. Since the unexpected formation of ββ′-dichloroethyl sulphide even in trifling amount is dangerous, sulphuric acid has been used as the catalyst in all esterifications.

than in the former experiment, the fraction b. p. 180—200°/23 mm. weighing 12 grams. No other fraction was obtained.

Condensation of $\beta\beta'$-Dichloroethyl Sulphide with Ethyl Sodioacetoacetate.

A cold solution of sodium ethoxide, prepared from 20 grams of sodium and 300 c.c. of absolute alcohol, was added to a mixture of 50 c.c. of $\beta\beta'$-dichloroethyl sulphide and 120 c.c. of ethyl acetoacetate. There was a slight evolution of heat, and the reaction was facilitated by shaking. The contents of the flask set to a white mass in half an hour, and, after remaining overnight, the reaction was completed on the water-bath, the alcohol removed, water added, and the mixture distilled in a current of steam. The heavy oil, non-volatile in steam, was extracted with ether, dried, and found to weigh 127 grams (120 c.c.). It decomposed on attempted distillation under diminished pressure.

Hydrolysis of the Ethyl Acetoacetate Derivative with Alkali.

The 127 grams of the above ester were slowly added to 430 c.c. of 20 per cent. methyl-alcoholic sodium hydroxide. Frothing took place, but the hydrolysis was not nearly so vigorous as in the case of the condensation product from ethyl malonate. The hydrolysis was completed by boiling for six hours on the water-bath, and the acetone methyl and ethyl alcohols were distilled off, the mass of sodium salt being extracted with ether (extract *A*) to remove any thioketone, and then acidified by the addition of 350 c.c. of concentrated hydrochloric acid. An oil was precipitated, which was extracted three times with ether, the ethereal solution being dried and evaporated. The brown acid weighed 47 grams, and began to crystallise after remaining at 0° in a vacuum over phosphoric oxide. The acid was esterified by boiling for three hours with 150 c.c. of alcohol and 15 c.c. of sulphuric acid, and yielded 40 grams of ester, which gave 19 grams of a fraction boiling at 184—192°/11 mm., mostly at 185°, and having n_D^{20} 1·4699. The residual, viscous ester in the flask began to decompose on attempted distillation (Found: S=12·6. $C_{12}H_{22}O_4S$ requires S=12·2 per cent.). On hydrolysis, the ester furnished γ-thiodibutyric acid, identical with that obtained from ethyl malonate, as shown by a mixed melting-point determination.

The methyl ester was prepared from the crude acid in order to obtain an ester with lower boiling point, and thus, so far as possible, to avoid decomposition on distillation. There was still,

however, a large amount of residual ester, which could not be distilled, and the yield of methyl ester was the same as that of the ethyl ester. *Methyl γ-thiodibutyrate* boils at 170°/20 mm., has n_D^{20} 1·4791, and is similar in properties to the ethyl ester:

0·2465 gave 0·2497 $BaSO_4$. S=13·9.

$C_{10}H_{18}O_4S$ requires S=13·7 per cent.

The ethereal extract (*A*) contained a small quantity of an oil with an odour not unlike peppermint. There was, however, insufficient of this by-product, probably the thiodiketone,

$$S(CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3)_2,$$

for its examination.

Two modifications of the ethyl acetoacetate condensation were tried. In the first case, no alcohol was used, the ethyl sodioacetoacetate being in suspension and solution in benzene. In the second case, the sodium ethoxide was added to the dichloro-derivative mixed with one-half the quantity of ethyl acetoacetate used in the preceding experiments. After remaining for three hours in the cold, when some salt was deposited, the remaining half of the ethyl acetoacetate was added, and the product worked up after remaining overnight. Ethyl γ-thiodibutyrate alone was isolated. This confirms the common observation that the tendency to form the ring or open chain is not dependent on the relative amounts of the dihaloid and ethyl sodioacetoacetate.

In these last two experiments, the condensation product was not distilled in a current of steam, and, with this exception, was worked up as before. The only ester obtained, however, was ethyl γ-thiodibutyrate.

The Action of ββ′-Dichloroethyl Sulphide on Potassium Cyanide.

In studying this reaction, care was taken to carry it out under conditions as anhydrous as possible, absolute alcohol being used in order to reduce the hydrolytic action of the potassium cyanide to a minimum. Thirty-five grams of finely powdered potassium cyanide (about 30 per cent. excess) were mixed with 250 c.c. of absolute alcohol, and 25 c.c. of ββ′-dichloroethyl sulphide added. No signs of a reaction were observed on shaking, but when the liquid was boiled, it soon turned brown, and white crusts, presumably of potassium chloride, adhered to the sides of the flask. The boiling was continued with occasional shaking for seven hours, and, while still hot, the alcoholic solution was filtered from insoluble inorganic matter. The precipitate was extracted with boiling alcohol and filtered, the filtrates mixed, and most of the alcohol distilled off. On cooling, the residual liquid set to a brown,

oily mass, which was collected and crystallised from methyl alcohol. Small, brown crystals formed which, on recrystallisation from acetone and then from benzene, melted at 87—88°, although the crystals were still slightly brown. The substance was obtained in colourless, microscopic crystals, melting at 91—91·5°, by dissolving in benzene, precipitating, and repeating this procedure several times.

The yield of this substance was poor, 25 c.c. (about 32 grams) of $\beta\beta'$-dichloroethyl sulphide furnishing 7 grams of the crude crystals melting at 87—88°. It is very readily soluble in methyl and ethyl alcohols, acetone, or benzene, moderately so in chloroform, and sparingly so in cold ether or light petroleum. It is insoluble in water, non-volatile in steam, and is rapidly hydrolysed by dilute boiling sodium hydroxide solution, ammonia being evolved in the process. It is insufficiently soluble in cold benzene or acetic acid for the molecular weight to be determined in these solvents by the cryoscopic method, and thus it became necessary to resort to naphthalene as a solvent, and also to the much less accurate ebullioscopic method:

0·1216 gave 0·2130 CO_2 and 0·0647 H_2O. C = 47·8; H = 5·9.
0·1152 „ 13·9 c.c. N_2 at 15° and 757 mm. N = 14·1.
0·3800 required 38·5 c.c. $N/10$-NaOH for hydrolysis. N(as NH_3) = 14·2.
0·2393 gave 0·5645 $BaSO_4$. S = 32·4.
0·376 in 17·83 naphthalene gave $\Delta^t = -0\cdot70°$. M.W. = 206.

The elevation of the boiling point of ethyl alcohol gave values for the molecular weight varying between 180 and 220.

$C_8H_{12}N_2S_2$ requires C = 48·0; H = 6·0; N = 14·0; S = 32·0 per cent. M.W. = 200.

On hydrolysis with dilute alkali, this nitrile was quantitatively converted into the corresponding acid, which was surprisingly sparingly soluble in cold organic solvents, except methyl and ethyl alcohols. It was moderately soluble in boiling xylene, and very rapidly precipitated on cooling. When dissolved in hot water and the solution cooled, the acid very slowly crystallised in pearly leaves which melted at 151—153°. This acid, like γ-thiodibutyric acid, was sparingly soluble in cold water:

0·1390 gave 0·2047 CO_2 and 0·0733 H_2O. C = 40·2; H = 5·9.
0·3733 „ 0·7175 $BaSO_4$. S = 26·4.
0·1650 neutralised 13·9 c.c. $N/10$-NaOH. Equiv. = 119.

$C_8H_{14}O_4S_2$ requires C = 40·3; H = 5·9; S = 26·9 per cent. Equiv. = 119.

As already mentioned, it is possible that the acid has the con-

stitution $CO_2H\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot CO_2H$, and it is hoped shortly to prepare an acid having the above formula.

Since $\beta\beta'$-dicyanoethyl sulphide had not been isolated, the attempt to prepare a six-membered ring containing five carbon atoms and one sulphur atom was relinquished.

1:4-*Thiazan*.

A mixture of 32 c.c. of $\beta\beta'$-dichloroethyl sulphide and 150 c.c. of freshly prepared 9 per cent. alcoholic ammonia was heated at 60° under pressure for four hours. By that time a mass of colourless crystals had separated, and the reaction was completed by heating at 100° for a further four hours. The crystals were washed out with a little water, in which they were very readily soluble, excess of ammonia was expelled by warming on the water-bath, and the brown solution acidified by hydrochloric acid. This liquid was then distilled in a current of steam in order to drive off alcohol and any unchanged $\beta\beta'$-dichloroethyl sulphide. After cooling, the contents of the flask were rendered strongly alkaline by means of sodium hydroxide, and a small quantity of oil separated. The alkaline solution was extracted fourteen times with ether, the ethereal solution dried and evaporated, and the residual red oil (15 grams) distilled. About 9 grams of a fraction boiling at 166—180°/758 mm. were collected, a large quantity of dark-coloured liquid being left in the distilling flask. On redistillation, 5 grams of a colourless liquid boiling at 168—170°/758 mm. were obtained. This was finally distilled over solid sodium hydroxide and boiled at 169°/758 mm.

1:4-*Thiazan* is a colourless liquid, miscible with water and organic solvents, and has an odour similar to, and yet more unpleasant than, that of pyridine. It is a very strong base, fumes in acid vapours, and very rapidly absorbs carbon dioxide from the air. When a drop was placed on a watch-glass, a scum was formed on its surface in a few seconds, and in the course of twenty minutes a non-deliquescent, white mass was produced, which dissolved with effervescence in dilute hydrochloric acid. Thiazan reacts vigorously with potassium on gentle warming, and hydrogen and a yellowish-brown solid are produced.

Thiazan boils at 169°/758 mm. and 166—167°/743 mm. It is noteworthy that this is slightly higher than the boiling point of the methyl derivative, namely, 163—164°/757 mm. (Clarke, *loc. cit.*, p. 1586):

0·1261 gave 0·2195 CO_2 and 0·0961 H_2O. C = 47·5; H = 8·45.
0·1641 „ 18·7 c.c. N_2 at 11° and 760 mm. N = 13·6.
0·1378 „ 0·3077 $BaSO_4$. S = 30·7.
C_4H_9NS requires C = 46·6; H = 8·7; N = 13·6; S = 31·1 per cent.

The *hydrochloride*, C_4H_9NS,HCl, was obtained in white clusters of needles by adding a solution of hydrogen chloride in benzene to a benzene solution of thiazan until the mixture was only faintly basic. This procedure was adopted because passing hydrogen chloride into a benzene solution of thiazan resulted in the needles at first formed being changed by the excess of acid to a yellow oil, insoluble in the benzene. This oil, on heating, gave off hydrogen chloride, and then, on cooling, the crystalline hydrochloride was regenerated. Probably the sulphur atom had developed latent basic properties and had taken up hydrogen chloride.

Thiazan hydrochloride, after being washed with benzene and dried in a vacuum over phosphoric oxide, was obtained in colourless, deliquescent crystals, which softened at 145° and melted at 160—165°:

0·2174 required 15·5 c.c. $N/10$-$AgNO_3$. Cl = 25·3.
0·2192 gave 17·5 c.c. N_2 at 11° and 760 mm. N = 9·5.
C_4H_9NS,HCl requires Cl = 25·45; N = 10·0 per cent.

The *platinichloride* was prepared by adding platinic chloride solution to thiazan dissolved in dilute hydrochloric acid, and slowly separated as a yellow precipitate, amorphous even when seen under the microscope. The precipitate was collected after remaining overnight, well washed with water, alcohol, and ether, and dried in a vacuum over phosphoric oxide and then at 70° in an air-oven. When dried at 100°, the platinichloride darkens and loses weight, although it does not melt below 250°. Owing to its insolubility, it could not be obtained crystalline:

0·1206 gave 0·0502 Pt. Pt = 41·6.
$C_4H_9NS,HCl,PtCl_4$ requires Pt = 40·9 per cent.

The *picrate* is best produced by adding a dilute solution of picric acid in alcohol to an alcoholic solution of thiazan. In this way, blunt, pale orange needles are rapidly formed, which, after being washed with alcohol and dried in a vacuum, are pure. If the base is added to the alcoholic solution of picric acid, the picrate is apt to separate at once as an amorphous, yellow precipitate, which is difficult to purify. The picrate is sparingly soluble in alcohol, but fairly readily so in acetone, and melts and decomposes at 198°:

0·3045 gave 0·2189 $BaSO_4$. S = 9·9.
$C_4H_9NS,C_6H_3O_7N_3$ requires S = 9·6 per cent.

The *picrolonate* was prepared in a similar way to the picrate, and crystallised from alcohol in deep orange, short prisms. It darkened somewhat at 210°, and melted and decomposed to a very viscous liquid at 242°:

0·2095 gave 0·1376 $BaSO_4$. S = 9·0.

$C_4H_9NS,C_{10}H_8O_5N_4$ requires S = 8·7 per cent.

The Ethiodide, $S<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>NH<\genfrac{}{}{0pt}{}{Et}{I}$.

It was thought of interest to see whether the sulphur atom in 1:4-thiazan would develop its higher valency as easily as the nitrogen. It was noticed that when ethyl iodide was added to thiazan, a clear solution was formed, which rapidly became cloudy and, on keeping, deposited colourless crystals. The experiment was repeated by adding to thiazan a large excess of ethyl iodide mixed with an equal volume of alcohol, heating to boiling, and then allowing the mixture to remain in a desiccator overnight. A small quantity of colourless crystals separated, more being obtained on partial evaporation of the alcoholic solution. The substance was extremely soluble in water, moderately so in hot 90 per cent. alcohol, and sparingly so in cold absolute ethyl and methyl alcohols or in boiling pyridine. Other ordinary organic solvents had no appreciable solvent action. The dried crystals darkened at about 230°, but did not melt below 260°:

0·0608 gave 0·0553 AgI. I = 49·1.

$C_6H_{14}NIS$ requires I = 49·4 per cent.

Only one molecule of ethyl iodide had therefore combined with one molecule of thiazan, the addition probably taking place at the nitrogen atom.

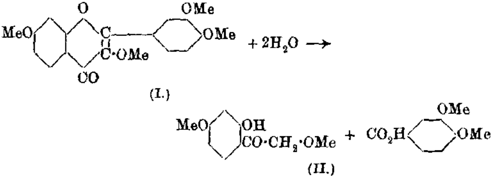
The author desires to express his gratitude to Prof. W. H. Perkin and Dr. E. Hope for the valuable advice he received from them in the course of this work. He also takes this opportunity of gratefully acknowledging a grant awarded him by the Board of Scientific and Industrial Research.

THE ORGANIC CHEMICAL LABORATORY,
OXFORD. [*Received, February* 19*th*, 1920.]

XXXVIII.—*Some Derivatives of Fisetol.*

By William Kershaw Slater and Henry Stephen.

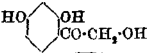
Fisetol dimethyl ether (II) was first isolated by Herzig (*Monatsh.*, 1891, **12**, 187) by boiling the tetramethyl ether of fisetin (I) with alcoholic potassium hydroxide, the dimethyl ether of protocatechuic acid being formed at the same time.



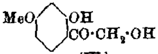
(I.) (II.)

In a similar way, the tetraethyl ether of fisetin was found to give fisetol diethyl ether corresponding with II. At the present time, no fisetol derivatives of the type containing a free hydroxyl group in the ω-position are known with certainty, and ω-hydroxy-resacetophenone (*fisetol*) (III), which possesses such a group, has not yet been described.

Tambor and Du Bois (*Ber.*, 1918, **51**, 748), however, claim to have isolated ω-2-dihydroxy-4-methoxyacetophenone (fisetol 4-methyl ether) (IV) from ω-bromoresacetophenone 4-methyl ether by conversion into the diacetate and subsequent hydrolysis of the latter.



(III.)



(IV.)

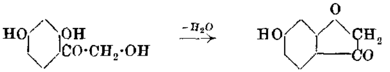
Sonn (*Ber.*, 1919, **52**, [*B*], 923) has cast some doubt on this result, and states that the product obtained by the action of acetic anhydride and sodium acetate on the corresponding ω-chloro-resacetophenone 4-methyl ether in the manner described by Tambor and Du Bois is the diacetate of 5-methoxycumaran-2-one. Auwers and Pohl (*Annalen*, 1914, **405**, 243) also obtained 5-methoxy-cumaran-2-one from the above chloro-compound by the action of hydrated sodium acetate in alcoholic solution.

It seems probable, also, that fisetol and derivatives of it containing a free hydroxyl group in the ω-position will resemble the parent substance, ω-hydroxyacetophenone (benzoylcarbinol), which is easily decomposed by warming in dilute acid or alkaline solutions.

This is shown also by Herzig's attempt to obtain fisetol by demethylation of the dimethyl ether (II) by treatment with hydriodic acid, which only resulted in the formation of tarry matter.

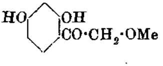
Difficulties originating from the above statements have been experienced in the present work, the object of which was an investigation of the synthesis of fisetol derivatives by a general method of preparation.

The method depends on the synthesis of aromatic ketones devised by Hoesch (*Ber.*, 1915, **48**, 1122), which is an extension of Gattermann's synthesis of aromatic aldehydes. Hoesch has shown that the condensation of a nitrile with a phenolic compound leads to the formation of a ketimine of the type CRR′:NH,HCl, which is easily hydrolysed to give the ketone, R·CO·R′. By condensing resorcinol with hydroxyacetonitrile, *5-hydroxycumaran-2-one* (V) is formed, and not fisetol, as would be expected. This fact imposes a limitation on the method, and from our experiments it appears that the method is limited by the presence of hydroxyl groups in the *ortho-* and *ω*-positions in the fisetol derivative formed in the reaction, a compound containing such groups being easily converted into the corresponding cumaran-2-one, as follows:

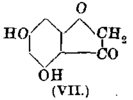


(V.)

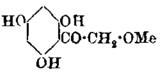
On the other hand, methoxyacetonitrile and resorcinol yield the stable fisetol derivative *ω-methoxyresacetophenone* (VI). Phloroglucinol, on treatment with the same nitriles, gave 3:5-dihydroxycumaran-2-one (VII) and *2:4:6-trihydroxy-ω-methoxyacetophenone* (VIII) respectively.



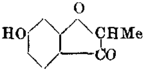
(VI.)



(VII.)



(VIII.)



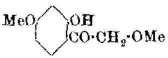
(IX.)

Acetaldehydecyanohydrin resembles hydroxyacetonitrile in its behaviour on condensation with resorcinol, yielding *5-hydroxy-1-methylcumaran-2-one* (IX).

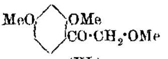
In carrying out the condensations, it was found that the presence of zinc chloride, as recommended by Hoesch, could be dispensed with, and it was only necessary to pass hydrogen chloride into a solution of methoxyacetonitrile and resorcinol in dry ether in order to bring about the formation of the crystalline ketimine hydrochloride, but the separation of the latter is only complete after the mixture has been allowed to remain for about five days in a refrigerator.

The condensations in which hydroxyacetonitrile and acetaldehydecyanohydrin were employed gave better results in the presence of zinc chloride, but the latter tends to cause decomposition during the isolation of the product unless considerable care is exercised. With reference to Hoesch's method, the preparation of resacetophenone has been repeated, using only resorcinol and acetonitrile in dry ether, and treating the resulting solution with dry hydrogen chloride. After remaining for five days in a refrigerator, the ketimine hydrochloride was decomposed in the usual way, and 94 per cent. of the theoretical yield of resacetophenone was obtained. Resorcinol dimethyl ether was found to give poor yields of 2:4-dimethoxyacetophenone, but these were much improved by the addition of zinc chloride to the mixture after treatment with hydrogen chloride, and then allowing to remain at the ordinary temperature for several days.

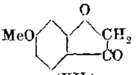
The following substances have been prepared in addition to those previously mentioned, and are described in a later part of the paper: 2-hydroxy-ω-4-dimethoxyacetophenone (fisetol dimethyl ether) (X), ω-2:4-trimethoxyacetophenone (fisetol trimethyl ether) (XI), 5-methoxycumaran-2-one (XII), and 5-methoxy-1-methylcumaran-2-one (XIII).



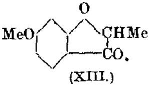
(X.)



(XI.)



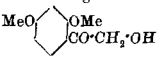
(XII.)



(XIII.)

The condensations of resorcinol dimethyl ether with hydroxyacetonitrile and acetaldehydecyanohydrin, respectively, yielded products which were not isolated in a pure condition. The ketimine which was formed in each case, on treatment with water and warming, gave a white solid, which easily decomposed on concentrating the solution to obtain a further quantity of material. The amounts

obtained were in each case too small for further investigation, but the properties of each substance closely resembled those of the corresponding ω-hydroxyacetophenone, and hence probably consisted of *ω-hydroxy-2:4-dimethoxyacetophenone* (XIV) and 2:4-dimethoxyphenyl α-hydroxyethyl ketone (XV). A brief description of the former only is given in the present paper, and both substances are being further investigated.



(XIV.)

(XV.)

Experimental.

Hydroxyacetonitrile, $HO \cdot CH_2 \cdot CN$.

The method described by Polstorff and Meyer (*Ber.*, 1912, **45**, 1911) for the preparation of hydroxyacetonitrile has been modified by substituting paraformaldehyde in place of commercial formaldehyde solution.

Potassium cyanide (32·5 grams: 1 mol.) was dissolved in water (100 c.c.), and paraformaldehyde (15 grams) added in small portions, the temperature of the solution being maintained between 0° and 5°. The paraformaldehyde dissolved, and, after the requisite amount had been added, the clear solution was allowed to remain for one hour. The odour of formaldehyde had entirely disappeared by this time, the solution being then treated according to the method described by Polstorff and Meyer. Hydroxyacetonitrile was subsequently extracted from the aqueous solution by continuous extraction with ether in an apparatus designed for the purpose. The ethereal solution was dried with anhydrous sodium sulphate, two-thirds of the ether removed by distillation from a water-bath, and the remainder evaporated under diminished pressure. Slight decomposition takes place if the whole of the ether is removed on the water-bath. Pure hydroxyacetonitrile (29 grams) was obtained, which distilled at 102°/14 mm.

Methoxyacetonitrile, $MeO \cdot CH_2 \cdot CN$.

Hydroxyacetonitrile, prepared as described above, was methylated by means of methyl sulphate according to the conditions given by Polstorff and Meyer (*loc. cit.*). The product boiled at 120°, and the yield from 15 grams of formaldehyde was 27 grams of the pure substance.

ω-Methoxyresacetophenone (Fisetol Methyl Ether) (VI).

Resorcinol (6·5 grams: 1 mol.) was dissolved in ether which had been previously dried (50 c.c.), and methoxyacetonitrile (5 grams:

1 mol.) added. A current of dry hydrogen chloride was passed through the solution for two hours, which was then allowed to remain overnight. A yellow, crystalline mass separated, consisting of the hydrochloride of the ketimine, and it was found in later experiments that the yield of this substance is increased by keeping the mixture for about five days in a refrigerator. The ether was poured off from the crystals, and the latter were washed twice with small quantities of dry ether and then dissolved in methyl alcohol, from which the ketimine hydrochloride separated as a fine, white, crystalline mass melting and decomposing at 205—207°:

0·1583 gave 9·2 c.c. N_2 (moist) at 17° and 753 mm. N = 6·67.

$C_9H_{11}O_3N,HCl$ requires N = 6·45 per cent.

The hydrochloride of the ketimine was dissolved in water and the solution warmed at 80° for half an hour, the colour changing to a claret-red; further heating caused a darkening of the solution with separation of tarry matter. At the end of the prescribed time, the solution was cooled, when a mass of crystals separated, and, after filtering and drying, the yield amounted to 8 grams, or about 70 per cent. of the theoretical. The substance crystallised from hot water in plates possessing a nacreous lustre, and melted at 136°. It is readily soluble in methyl or ethyl alcohols, ether, or benzene, and insoluble in light petroleum. With ferric chloride it gives a deep violet coloration, and reduces Fehling's solution, with the formation of a copper mirror. Tollens's reagent is also immediately reduced, with the precipitation of metallic silver:

0·1234 gave 0·2712 CO_2 and 0·0647 H_2O. C = 59·98; H = 5·82.

$C_9H_{10}O_4$ requires C = 59·91; H = 5·5 per cent.

The p-*nitrophenylhydrazone* was obtained by adding a solution of *p*-nitrophenylhydrazine in dilute acetic acid to an aqueous solution of ω-methoxyresacetophenone. The hydrazone soon separated as a flocculent, yellow mass, which was immediately collected, and, after crystallisation from hot water containing a little ethyl alcohol, it melted and decomposed at 205°. On remaining in the air for several days, it becomes brick-red:

0·1596 gave 18·2 c.c. N_2 (moist) at 19° and 769 mm. N = 13·4.

$C_{15}H_{15}O_5N_3$ requires N = 13·25 per cent.

2-*Hydroxy-ω-4-dimethoxyacetophenone* (X).

By methylating 1·8 grams of the compound described above with 1·2 grams (1 mol.) of methyl sulphate in 10 c.c. of 5 per cent. sodium hydroxide solution and keeping the solution cold in ice-water, acidifying with dilute hydrochloric acid, and concentrating, 1·5 grams of the monomethyl ether were obtained. After crystal-

lising from dilute alcohol, it was deposited in clusters of fine needles melting at 66°. There was no trace of the isomeric 4-hydroxy-ω-2-dimethoxyacetophenone.

A similar case has been observed by Hoesch (*loc. cit.*), who found that, on methylating resacetophenone with one molecular proportion of methyl sulphate, a quantitative yield of paeonol was obtained. 2-Hydroxy-ω-4-dimethoxyacetophenone was also obtained in the following manner.

Resorcinol monomethyl ether (3·2 grams: 1 mol.) and methoxyacetonitrile (2·5 grams: 1 mol.) were dissolved in dry ether (25 c.c.), and the solution was treated with a rapid stream of hydrogen chloride for one hour. Zinc chloride (1 gram) was now added, and the mixture allowed to remain for three days. A red oil separated, from which the ether was decanted, and the oil was washed twice with small quantities of ether. On treatment with water, it dissolved, and on warming the solution, small, colourless needles soon deposited. These were collected and dried, and found to be identical with the substance prepared by methylation, as above. After crystallisation from methyl alcohol, the substance melted at 66°, which in both cases agrees with that found by Herzig (*loc. cit.*).

ω-2:4-Trimethoxyacetophenone (XI).

This compound was prepared according to the method stated by Herzig, by methylating the substance just described with methyl iodide and potassium hydroxide solution, and crystallised from alcohol in fine, silky needles melting at 61—62°. Methylation of ω-methoxyresacetophenone with two molecular proportions of methyl sulphate at 60° for eight hours produces the same substance, which separates from the alkaline solution. A higher temperature during the methylation causes much decomposition, with the formation of tarry material.

We have succeeded in preparing the above substance by condensing resorcinol dimethyl ether with methoxyacetonitrile. The process is similar to that already described. The yield, however, is poor: 5 grams of the dimethyl ether and 2·5 grams of the nitrile gave 1·4 grams of the product, that is, about 16 per cent. of the theoretical.

5-Hydroxycumaran-2-one (V).

This substance was prepared by treating 3 grams (1 mol.) of hydroxyacetonitrile and 5·5 grams (1 mol.) of resorcinol dissolved in 30 c.c. of dry ether to which a little zinc chloride was added. On passing a current of dry hydrogen chloride through the solution, a crystalline deposit separated after fifteen minutes, and after twenty-four hours the mixture was treated in the usual way.

The product, after crystallisation from hot water, in which it is sparingly soluble, was obtained in thin plates, which melted and decomposed at 240°, and gave no coloration with ferric chloride. (Found: C = 63·74; H = 4·06. $C_8H_6O_3$ requires C = 64·0; H = 4·0 per cent.). The compound has already been described by Brühl and Friedländer (*Ber.*, 1897, **30**, 299). It reduces Fehling's solution in the cold, and with Tollens's reagent gives a silver mirror on warming.

On treatment with acetyl chloride (1 mol.), the acetyl compound was produced, which crystallised from dilute alcohol in leaves melting at 81°.

5-Methoxycumaran-2-one (XII).

All attempts to methylate 5-hydroxycumaran-2-one were unsuccessful, the action of methyl sulphate and of methyl iodide in alkaline solution producing a viscid, resinous mass. It was ultimately prepared by condensing resorcinol monomethyl ether with hydroxyacetonitrile, and was the only product isolated from the reaction. No trace of ω-4-dihydroxy-2-methoxyresacetophenone was found in the aqueous solution after the separation of 5-methoxycumaran-2-one, and rather less than a gram of the latter was obtained from 4 grams (1 mol.) of the ether and 2·5 grams (1 mol.) of nitrile. It crystallises from hot alcohol in pale straw-coloured needles melting at 120°, and has been fully described by Blom and Tambor (*Ber.*, 1905, **38**, 3589), Auwers and Pohl (*Annalen*, 1914, **405**, 264), and Sonn (*loc. cit.*).

ω-Hydroxy-2:4-dimethoxyacetophenone (XIV).

The condensation of hydroxyacetonitrile with resorcinol dimethyl ether according to Hoesch's method gave a crystalline deposit when hydrogen chloride was passed into an ethereal solution of the two compounds. The deposit was dissolved in water, the solution concentrated by warming on the water-bath for a quarter of an hour, and finally by allowing to remain in a desiccator for two days. A fine, yellow, crystalline substance was deposited which after being collected, was found to be only sparingly soluble in water, but readily so in alcohol. The dilute aqueous solution reduced Fehling's solution in the cold, giving cuprous oxide, and Tollens's reagent gave a precipitate of metallic silver. On boiling the substance with water, it appeared to be volatile in steam, crystalline deposit being observed on the cool sides of the tube. On prolonged boiling (about five minutes), decomposition took place with the formation of an oily scum. This decomposition occurred almost immediately in the presence of hydrochloric acid or sodiu

hydroxide. The purest sample of the compound obtained melted and decomposed at 127—129°, but there was insufficient for an analysis.

2:4:6-*Trihydroxy-ω-methoxyacetophenone* (VIII).

This substance was readily obtained from the condensation of methoxyacetonitrile and anhydrous phloroglucinol in the usual way. The intermediate ketimine hydrochloride was isolated as a white, crystalline powder after crystallisation from methyl alcohol, which decomposed without melting between 238° and 241°. On boiling it with water, a clear solution was obtained, from which fine, silky needles separated on cooling. These were collected and recrystallised from hot water, and after drying in the air for several days assumed a pink tinge and appeared to effloresce. A sample dried at 100° melted at 192°, and its aqueous solution gave a violet coloration with ferric chloride:

0·1288 gave 0·2355 CO_2 and 0·0681 H_2O. C=49·87; H=5·89.
$C_9H_{12}O_6$ requires C=50·0; H=5·6 per cent.

0·2451, on heating at 100° for two hours, lost 0·0203. H_2O=8·0.
$C_9H_{10}O_5,H_2O$ requires H_2O=8·3 per cent.

On treatment with *p*-nitrophenylhydrazine in dilute acetic acid solution, a pale yellow, flocculent precipitate was obtained, which rapidly darkened in colour, finally assuming a chocolate-brown, and it was apparent that oxidation had taken place. The hydrazone was not obtained in a condition of sufficient purity for a melting-point determination or analysis.

Methylation of the above trihydroxy-compound with methyl sulphate gave ω-2:4:6-tetramethoxyacetophenone, which has been described by Herzig and Hofmann (*Ber.*, 1909, **42**, 155), who obtained it by methylating 6-hydroxy-ω-2:4-trimethoxyacetophenone, the latter being isolated as a decomposition product from the action of alcoholic potassium hydroxide on the pentamethyl ether of morin.

The trihydroxy-compound (1·5 grams) was dissolved in 20 c.c. of sodium hydroxide solution containing 2 grams (6 mols.) of sodium hydroxide, and 4·2 grams (3·5 mols.) of methyl sulphate were added with vigorous stirring, rise in temperature being avoided. An oil soon separated, and, on cooling in ice-water, solidified to a pasty, crystalline mass, which was well drained. After crystallisation from methyl alcohol, the pure substance melted at 50°, and gave no coloration with ferric chloride (Found: C=59·86; H=6·81. $C_{12}H_{16}O_5$ requires C=60·0; H=6·66 per cent.).

3 : 5-*Dihydroxycumaran-2-one* (VII).

This substance has already been described by Sonn (*Ber.*, 1917, **50**, 1265). As previously stated, the same substance was prepared by the condensation of anhydrous phloroglucinol with hydroxyacetonitrile. The ketimine hydrochloride which separated during the reaction was dissolved in water, and the solution warmed on the water-bath for half an hour. On cooling the red-coloured solution, crystals soon deposited, which, after being collected and washed with a little light petroleum, were only faintly red, and on crystallisation from hot water the pure substance was obtained in colourless plates, melting at 248° to a dark red liquid. An aqueous solution of the substance gave a purple coloration with ferric chloride.

The diacetyl compound was prepared by treating the substance with a few drops of pyridine, and then adding a slight excess of acetyl chloride. The mixture was warmed on the water-bath for one minute and then treated with water, and the oil which separated soon solidified. After crystallising the solid from methyl alcohol, it melted at 122°, and consisted of small, prismatic needles.

5-*Hydroxy*-1-*methylcumaran-2-one* (IX).

Resorcinol (5·6 grams : 1 mol.) was dissolved in dry ether (25 c.c.), acetaldehydecyanohydrin (3·3 grams : 1 mol.) added, and a current of dry hydrogen chloride passed into the solution for three hours. The ketimine hydrochloride separated during the process, and the quantity was increased by allowing the mixture to remain in a refrigerator for several days. The pale red, crystalline mass (about 8·5 grams) was dissolved in ice-water, and the solution carefully neutralised with solid sodium hydrogen carbonate, when the ketimine was precipitated as a pale yellow solid (6 grams):

0·1490 gave 10·4 c.c. N_2 (moist) at 18° and 750 mm. N = 8·15.

$C_9H_9O_2N$ requires N = 8·58 per cent.

The ketimine was soluble in water or sodium hydroxide solution on warming, and in both cases the solutions became deep red, and ammonia was simultaneously evolved. The aqueous solution, on cooling, deposited a straw-coloured, crystalline powder, which proved to be 5-hydroxy-1-methylcumaran-2-one. The base is soluble in hot methyl or ethyl alcohols, and crystallises from the latter in faintly yellow, small prisms melting at 152°. It is insoluble in benzene and sparingly soluble in ethyl acetate or acetone. Attempts to prepare a platinum salt were not successful, and resulted in the formation of tarry material, probably caused by oxidation.

The aqueous solution reduces Fehling's solution and Tollens's reagent.

As stated above, on boiling the aqueous solution of the ketimine, the corresponding cumaranone derivative was obtained, which crystallised from hot alcohol in prisms. The latter are sparingly soluble in hot water, soluble in sodium hydroxide solution, giving a yellow coloration, and also in hydrochloric acid, producing a deep red colour. The substance begins to decompose at 233° and melts and decomposes completely at 238—240°.

The aqueous solution of the cumaranone reduces silver nitrate solution, with the deposition of a silver mirror, and Fehling's solution is reduced on gentle warming, a precipitate of cuprous oxide being produced:

0·1160 gave 0·2800 CO_2 and 0·0514 H_2O. C=65·80; H=4·92.

$C_9H_8O_3$ requires C=65·85; H=4·87 per cent.

Methylation of the above compound with methyl sulphate was unsuccessful, and resulted in the formation of a dark-coloured oil, which was difficult to purify.

5-*Methoxy*-1-*methylcumaran*-2-*one* (XIII).

Auwers and Müller (*Ber.*, 1917, **50**, 1172) have already described the properties of this compound, but the following method of preparation of it is different from that employed by these investigators. Resorcinol monomethyl ether (2·5 grams: 1 mol.) and acetaldehydecyanohydrin (1·5 grams: 1 mol.) were treated with hydrogen chloride in dry ethereal solution. At the end of an hour, 0·5 gram of zinc chloride was added, and the mixture allowed to remain at the ordinary temperature for two days. A red oil separated from the ether, and the latter was then decanted and the oil washed several times with small quantities of dry ether. On pouring into water, a clear solution was obtained, which, however, became cloudy on warming and a colourless oil separated. This solidified on cooling, and the solid crystallised from methyl alcohol in long, thin needles melting at 60°.

The present investigation is being continued on similar lines, and in concluding this paper we desire to thank Prof. Lapworth for the interest he has taken in the work, and also for placing various materials at our disposal.

The Chemical Laboratories,
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Manchester. [*Received, February 6th*, 1920.]

XXXIX.—*The Effect of Heating on the Absorptive Power of Sugar-charcoal for Sulphur Dioxide.*

By Ramsay Middleton Winter and Herbert Brereton Baker.

During the later stages of the war the absorptive power of charcoal for poisonous gases and lachrymatory vapours was of the greatest importance. In the earlier types of box respirators animal-charcoal was employed, but when the use of this type of respirator was extended to all troops, it became necessary to investigate other kinds of charcoal, of which an unlimited amount would be available. Experiments carried on at the Imperial College, chiefly by Prof. Philip, showed that, contrary to the earlier belief, wood-charcoal which had been subjected to long-continued heating gained so much in absorptive power that, in this respect, it was in no way inferior to animal-charcoal.

It was thought worth while to investigate this question further, using the purest charcoal obtainable, and incidentally to find out whether this increase in absorptive power was associated with any other changes in the physical properties of the charcoal.

The sugar-charcoal was prepared by heating the finest crystallised sugar until no fumes or odour were perceptible. After roughly powdering the mass, it was placed in a hard-glass flask, in which it was heated in a vacuum. Chlorine was then admitted and allowed to remain all night. The flask was next heated to redness for half an hour, a vacuum being maintained in it by means of a good water-pump. The charcoal on boiling with water gave no indication of the presence of chlorine or hydrochloric acid. It was heated in a muffle furnace for half an hour, powdered, and sieved. The particles between 0·4 and 0·8 mm. in diameter were used in the experiments.

The ash from different samples showed a very uniform percentage, 0·113 being the mean value.

Specific Gravity of the Charcoal.—The material which had been heated to about 900° in a muffle furnace for four hours had a specific gravity of 1·76, mean of six samples.

That which had been heated for forty hours had a specific gravity of 1·84, mean of two samples.

Absorptive Power of the Charcoal.—Sulphur dioxide was chosen for the first experiments, since the gas is easily obtained in a fairly pure state from the liquefied substance, and also because the amount absorbed is very considerable.

The gas was contained in a gas-burette over mercury, which, with its accompanying barometer tube, was surrounded by a jacket

through which water at a constant temperature was circulated. Sealed on to its exit-tube a long capillary tube communicated, by means of a mercury-protected ground joint, with the thick hard-glass bulb in which the charcoal was placed. It was found impossible to weigh the charcoal in an open weighing tube, so rapid was its absorption of water vapour from the air. No lubricator was used for the ground joint. By means of a screw clamp on each side the parts of the joint were kept in close contact, and no leakage occurred when, as sometimes happened, there was a considerable internal pressure. Before admitting the sulphur dioxide, the bulb containing the weighed charcoal was exhausted by means of a Gaede pump, and heated to redness for two hours. It was then cooled in a bath containing melting ice, the same water, at 0°, being circulated through the jacket of the gas-burette. The latter, which had a volume of about 100 c.c., had been carefully calibrated, and the volume of the bulb had been determined by weighing its volume of mercury. It was feared that the volume of the bulb might change on heating when exhausted. This was not found to be the case when the bulb was of sufficient thickness.

On admission of the sulphur dioxide the absorption was very rapid for the first hour. It then became extremely slow, but in seventy-two hours no further absorption could be measured. The results obtained were, with 1 gram of charcoal which had been heated previously for the times stated:

Hours	4	40	42½	45½
C.c.	97	195	241	288

Saussure (*Ann. Physik.* [Gilbert], 1814, **47**, 113) found that one volume of charcoal of sp. gr. 1·57 absorbed sixty-five volumes of sulphur dioxide, or 1 gram of charcoal absorbed 38 c.c. of sulphur dioxide.

Favre (*Ann. Chim. Phys.*, 1871, [iv], **24**, 247), with charcoal of the same specific gravity, found that 1 gram absorbed 105 c.c. of the gas.

Conclusion.

Charcoal, in a very pure form, has its specific gravity increased by forty hours' heating to 900° from 1·76 to 1·84. By the same treatment the amount of sulphur dioxide absorbed is increased from 97 c.c. to 288 c.c.

It is proposed to extend this investigation to the cases of other gases, and also to find if other physical properties of charcoal are affected by prolonged heating.

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[*Received, March 3rd, 1920.*]

XL.—*Compounds of Thiocyanates of certain Bivalent Metals and Hydrazine.*

By Priyadaranjan Rây and Pulin Vihari Sarkar.

It has already been shown (Curtius and Schrader, *J. pr. Chem.*, 1894, [ii], **50**, 311; Hofmann and Marburg, *Ber.*, 1897, **30**, 2019; Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1909, **60**, 247; Franzen and Lucking, *ibid.*, 1911, **70**, 145) that hydrazine gives compounds with various metallic salts similar to those formed by ammonia, and in the present paper compounds of hydrazine with the thiocyanates of nickel, cobalt, zinc, cadmium, and manganese are described. These compounds are closely related as regards their chemical and physical properties. They are all sparingly soluble in water, the nickel compound being the least soluble. Hence they have all been prepared by the addition of an ammoniacal hydrazine sulphate solution to the solution of any of the metallic salts in the presence of sufficient ammonium thiocyanate. The nickel and cobalt compounds possess very characteristic colours. They are all crystalline, and, with the exception of the nickel compound, all are decomposed by hot water into the corresponding metallic hydroxides; the manganese compound is immediately decomposed even by cold water, but in the presence of sufficient ammonium thiocyanate solution and hydrazine they can be preserved in cold water without any decomposition for a long time, air being carefully excluded in the case of the manganese compound. The nickel salt is very stable, and is not decomposed by boiling with water for a long time or by heating at 150° in the dry state. Cobalt stands next to nickel as regards stability. Judging from the marked change in the solubility of these compounds, and in the colour of the nickel and cobalt compounds, from those of their constituents, both the thiocyanates of the above metals and hydrazine being freely soluble in water, it can be safely asserted that complex ions are formed, and this has been conclusively proved by determining the conductivity of the nickel compound. The molecular conductivity was found to be 210·4, a value which indicates the presence of three ions and closely approaches those determined by Werner and Miolati (*Zeitsch. physikal. Chem.*, 1893, **12**, 34; 1894, **14**, 506) for complex ammonia salts of platinum, cobalt, and chromium. The values obtained by them for the molecular conductivity of those salts which yield two free ions in addition to the complex ion range from 234·4 to 267·6. The composition and

constitution of these compounds are therefore represented by the general formulæ $R(SCN)_2,2N_2H_4$ and $[R(N_2H_4)_2]^{\cdot\cdot}(SCN)'_2$, where R stands for Ni, Co, Zn, Cd, or Mn.

EXPERIMENTAL.

Compound of Nickel Thiocyanate and Hydrazine.—A solution of nickel sulphate was mixed with a concentrated solution of ammonium thiocyanate, and an ammoniacal solution of hydrazine sulphate was added. A voluminous violet-blue powder was precipitated, which was washed with water and dried in a vacuum. The substance is crystalline and very sparingly soluble in water, 100 grams dissolving 0·079 gram at 30°. It is not appreciably changed by cold dilute ammonia or acids, but on heating with the latter it decomposes and passes into solution, and with hot ammonia it becomes soluble, forming the blue nickel–ammonia cation:

0·1631 gave 0·0512 NiO. Ni = 24·7.

0·1097 „ (after oxidation with bromine) 0·2150 $BaSO_4$. S = 26·9.

0·0263, on treatment with alkaline ferricyanide (Rây and Sen, *Zeitsch. anorg. Chem.*, 1912, **76**, 380), gave 5·8 c.c. N_2 at 30° and 753·6 mm. N_2H_4 = 26·9.

$Ni(SCN)_2,2N_2H_4$ requires Ni = 24·6; S = 26·85; N_2H_4 = 26·85 per cent.

A solution of the substance in conductivity water was obtained by shaking for several hours at 24·5°. The resistance was found to be 1600 ohms. The strength of the solution was 0·0128 per cent., the cell constant 0·169, and hence the molecular conductivity = 210·4 at 24·5°.

Compound of Cobalt Thiocyanate and Hydrazine.—A solution of cobalt chloride was employed, and the same procedure was followed as in the case of the nickel compound. A voluminous, flesh-coloured powder was precipitated, which was washed with aqueous alcohol, then with absolute alcohol, and dried in a vacuum. The dry substance is fairly stable, decomposing at about 150° into black cobalt oxide. On heating with water, the substance decomposes, with the formation of cobaltous hydroxide. It is soluble both in dilute ammonia and dilute acids:

0·2511 gave 0·0623 Co. Co = 24·8.

0·1446 „ 0·2817 $BaSO_4$. S = 26·74.

0·0239 „ 5·3 c.c. N_2 at 30° and 750·06 mm. N_2H_4 = 26·9.

$Co(SCN)_2,2N_2H_4$ requires Co = 24·7; S = 26·8; N_2H_4 = 26·8 per cent.

Compound of Cadmium Thiocyanate and Hydrazine.—A concentrated solution of cadmium chloride was employed, and the same

procedure was followed as described above. A white, crystalline precipitate was obtained, which was collected, washed with alcohol, and dried in a vacuum. The substance decomposes into cadmium hydroxide on heating with water. It is soluble in dilute ammonia or dilute acids:

0·0563 gave 0·0404 $CdSO_4$. Cd = 38·6.

0·1346 ,, 0·2139 $BaSO_4$. S = 21·81.

0·0541 ,, 9·7 c.c. N_2 at 30° and 757·9 mm. N_2H_4 = 22·05.

$Cd(SCN)_2,2N_2H_4$ requires Cd = 38·44; S = 21·9; N_2H_4 = 21·9 per cent.

Compound of Zinc Thiocyanate and Hydrazine.—The same method of preparation was followed with a concentrated solution of zinc chloride. A white, crystalline precipitate was obtained, which was washed with alcohol and dried in a vacuum. On heating with water, the substance decomposes into zinc hydroxide. It is stable in the dry state, and soluble in dilute ammonia or dilute acids:

0·1520 (after oxidation with bromine and subsequent precipitation as basic carbonate) gave 0·0511 ZnO. Zn = 26·96.

0·0584 gave 0·1114 $BaSO_4$. S = 26·17.

0·0342 ,, 7 c.c. N_2 at 27° and 760·5 mm. N_2H_4 = 25·7.

$Zn(SCN)_2,2N_2H_4$ requires Zn = 26·65; S = 26·1; N_2H_4 = 26·1 per cent.

Compound of Manganese Thiocyanate and Hydrazine.—A concentrated solution of manganese chloride was employed. The substance was obtained as a white, crystalline precipitate, which was washed with absolute alcohol and dried in a vacuum. It readily decomposes on contact with cold water, with the formation of brown, manganic hydroxide. In the dry state, the substance is fairly stable. It is soluble in dilute acids, and decomposes in the presence of dilute ammonia into manganic hydroxide:

0·1408 gave 0·0909 $MnSO_4$. Mn = 23·52.

0·1309 ,, 0·2542 $BaSO_4$. S = 26·66.

0·0336 ,, 7·25 c.c. N_2 at 28° and 761·7 mm. N_2H_4 = 27·19.

$Mn(SCN)_2,2N_2H_4$ requires Mn = 23·43; S = 27·2; N_2H_4 = 27·2 per cent.

Our best thanks are due to Prof. Sir P. C. Rây for his kind encouragement.

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XLI.—*Some Condensations of* n-*Butyl Alcohol and* n-*Butaldehyde.*

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n-BUTYL ALCOHOL and *n*-butaldehyde are substances on which little work has been done beyond the preparation of the ordinary derivatives and the elucidation of their general properties.

n-Butyl alcohol is now, however, obtainable in large quantities, being a by-product in the new process for obtaining acetone, namely, by the fermentation of natural products containing starch by members of the group of organisms included under the generic name *Bacillus amylobacter*. The fermentation gives rise to acetone and *n*-butyl alcohol in the proportion of one part of acetone to two of *n*-butyl alcohol, together with a large volume of gas, consisting approximately of a mixture of equal volumes of hydrogen and carbon dioxide.

The production by this method of large quantities of *n*-butyl alcohol invited experimental work in a number of directions, and of these, the condensations of *n*-butyl alcohol and *n*-butaldehyde are not the least important.

n-Butaldehyde is readily obtainable from *n*-butyl alcohol by direct oxidation, but the yields are poor, being less than 30 per cent., most of the alcohol being converted into *n*-butyl *n*-butyrate and tarry matter.

The method adopted to prepare *n*-butaldehyde in quantity was that of Bouveault, using a copper catalyst at 300°, an almost theoretical yield of aldehyde from alcohol being obtained.

n-Butaldehyde readily undergoes the "aldol" condensation, giving a 60—70 per cent. yield of the aldol,

$$OH\cdot CHPr^{\alpha}\cdot CHEt\cdot CHO,$$

which on distillation under the ordinary pressure loses water, giving α-ethyl-Δ^{α}-hexenealdehyde, $CHPr^{\alpha}\colon CEt\cdot CHO$, and this, on complete reduction with aluminium amalgam and water, gives α-ethylhexyl alcohol, $CH_2Pr^{\alpha}\cdot CHEt\cdot CH_2\cdot OH$.

On oxidation with silver oxide and barium hydroxide, α-ethyl-Δ^{α}-hexenealdehyde gives an unsaturated acid, $CHPr^{\alpha}\colon CEt\cdot CO_2H$, which on reduction with zinc and sulphuric acid gives α-ethylhexoic acid, $CH_2Pr^{\alpha}\cdot CHEt\cdot CO_2H$.

Guerbet, in his work on the action of sodium on alcohols (*Compt. rend.*, 1901, **133**, 1220; 1902, **134**, 467), obtained from *n*-butyl alcohol an octyl alcohol, in every way similar to the above, to

which he gave the formula $CH_2Pr^a\cdot CHMe\cdot CH_2\cdot OH$. This would obviously be formed by the loss of water from two molecules, thus: $CH_2Pr^a\cdot\vdots OH\ \ H\vdots CHMe\cdot CH_2\cdot CH_2\cdot OH$, that is, it is the β-hydrogen atom that reacts. This seems improbable, owing to the superior activity of α-hydrogen atoms, and the reaction was investigated in order to discover the best conditions and also to establish the constitution of the octyl alcohol obtained.

The production of *n*-butyric acid by the interaction of *n*-butyl alcohol and sodium led to the investigation of the action of sodium hydroxide on *n*-butyl and ethyl alcohols.

The action of sodium on mixed *n*-butyl and ethyl alcohols was also tried, with results similar to those obtained with *n*-butyl alcohol, but with poor yields.

Action of Sodium on n-*Butyl Alcohol.*—Experiments were carried out with varying amounts of sodium and at varying temperatures. The products consisted of octyl alcohol, *n*-butyric acid, and some octoic acid, with traces of esters, ethers, and dodecyl alcohol.

In all cases, the amounts of octyl alcohol and *n*-butyric acid were proportional to the actual amount of sodium present, within small limits. The temperature at which the reaction was carried out had no effect, except on the time required to complete the reaction.

The equation which represents the reaction is as follows:

$$3C_4H_9\cdot OH + Na \longrightarrow C_8H_{17}\cdot OH + C_4H_7O_2Na + 5H.$$

Some of the *n*-butyric acid was always replaced by a little octoic acid, and similarly some *n*-butyl alcohol was always found unchanged.

The reaction evidently takes place in two stages, namely, (i) formation of octyl alcohol and sodium hydroxide,

$$C_4H_9\cdot OH + C_4H_9\cdot ONa = C_8H_{17}\cdot OH + NaOH,$$

and (ii) formation of acid from alcohol.

The sodium hydroxide formed in (i) then acts on unchanged *n*-butyl alcohol, giving *n*-butyric acid and hydrogen,

$$C_4H_9\cdot OH + NaOH = C_4H_7O_2Na + 4H.$$

The octoic acid obtained, and consequently the octyl alcohol, has the α-ethyl, and not the β-methyl, structure assigned to it by Guerbet. The constitution was established by a comparison of the amide with that of α-ethylhexoic acid prepared by Raper's method (T., 1907, **91**, 1837).

Action of Sodium Hydroxide on n-*Butyl and Ethyl Alcohols.*—This reaction is almost identical with the second part of the above reaction. In the case of *n*-butyl alcohol, about 80 per cent. of the sodium hydroxide is converted into sodium *n*-butyrate when excess

of alcohol is used, small quantities of α-ethylhexyl alcohol and α-ethylhexoic acid being also formed.

The action of sodium hydroxide on ethyl alcohol gives only poor yields of acetic acid, quantities of a brown, resinous substance being obtained, which appears to be akin to aldehyde resin.

The action of metallic calcium on *n*-butyl alcohol is similar to that of sodium, smaller yields of α-ethylhexyl alcohol being obtained, but very little *n*-butyric acid. This is borne out by the fact that calcium oxide and slaked lime when heated with *n*-butyl alcohol give only negligible quantities of *n*-butyric acid.

Action of Sodium on a Mixture of n-*Butyl and Ethyl Alcohols.*—A few experiments only were carried out, as the yields were poor, less than 20 per cent. of *n*-hexyl alcohol and *n*-hexoic acid being obtained.

The products were mainly α-ethylhexyl alcohol and *n*-hexoic acid, in addition to *n*-butyric acid. Very little *n*-hexyl alcohol was obtained. Other products were acetic acid and α-ethylhexoic acid.

The hexoic acid and hexyl alcohol have a normal chain of six atoms, and must therefore be formed thus:

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot \boxed{ONa \quad H}CH_2\cdot CH_2\cdot OH.$$

This points to the fact that when sodium is dissolved in a mixture of the alcohols, or when sodium ethoxide is dissolved in *n*-butyl alcohol, most of the sodium is present as *n*-butoxide and not as ethoxide. This bears out recent work on solutions of sodium hydroxide in ethyl alcohol, which are stated to contain most of the sodium as ethoxide.

The yields obtained here, although poor, were better than those obtained by Guerbet (*Compt. rend.*, 1902, **135**, 172) from heptyl and ethyl alcohols, in which case the yields of nonyl alcohol were only 3—5 per cent.

α-Ethylhexyl alcohol is readily dehydrated by heated aluminium oxide, giving theoretical yields of an *octylene*. This, when shaken with 90 per cent. sulphuric acid, gives a pleasant-smelling hydrocarbon having the same empirical formula, which is probably a *dioctylene*.

Condensations of n-*Butaldehyde and* n-*Butyl Alcohol with Acetone.*—*n*-Butaldehyde readily condenses with acetone when treated with alkali hydroxides. With 10 per cent. potassium hydroxide it gives an aldol, $OH\cdot CHPr^{\alpha}\cdot CH_2\cdot COMe$, which on distillation gives Δ^{γ}-*heptylene-β-one* (n-*butylideneacetone*),

$$CHPr^{\alpha}:CH\cdot COMe.$$

By passing *n*-butaldehyde and acetone over aluminium oxide, some *n*-butylideneacetone was obtained, but the main products were hydrocarbons of low boiling points.

n-Butylideneacetone undergoes changes when heated with sodium hydrogen sulphate or sulphuric acid, and when passed over heated copper, which suggests the formation of ring compounds, but no definite results have been obtained at present.

n-Butyl alcohol and acetone when passed over heated aluminium oxide lose water, giving a complex mixture of products from which methyl amyl ketone and a *heptadiene*, C_7H_{12}, have been isolated; traces of *n*-butaldehyde and *iso*propyl alcohol are also present.

Other products are probably an unsaturated alcohol, isomeric with methyl amyl ketone, and the hydrocarbon derived from it, possibly allylene or allene, and other hydrocarbons and various oils of high boiling points which have not been identified.

The reaction is probably mainly $CH_2Pr^{a}\cdot$ OH H $CH_2\cdot COMe$, giving methyl amyl ketone, and CMe_2 O H_2 $CEt\cdot CH_2\cdot OH$, giving an unsaturated alcohol, both the ketone and alcohol undergoing further dehydration, yielding hydrocarbons.

EXPERIMENTAL.

n-*Butyl Alcohol.*

Starch, and carbohydrates in general, when fermented by members of the group *Bacillus amylobacter*, give rise to acetone and *n*-butyl alcohol.

About 25 per cent. of the starch is lost as a mixture of hydrogen and carbon dioxide in equal proportions, and about 25 per cent. is found in the fermented "wash" as acetone (8—9 per cent. on the starch) and *n*-butyl alcohol (16—17 per cent. on the starch), together with a little *iso*propyl alcohol, probably formed by the reduction of some of the acetone by the hydrogen present. The bacillus is anærobic, the fermentation being complete in from twenty-four to thirty hours, according to conditions. Traces of acid are formed, which suggests that hydroxybutyric acid is an intermediate product.

The fermented "wash" is distilled, and the "oil" salted out from the distillate with potassium carbonate; on distillation, the oil is fractionated as below:

Typical Distillation of 500 *Grams of "Oil."*

55—60°	126 grams	85— 90°	4 grams.
60—65	2 ,,	90— 95	58 ,,
65—70	1 ,,	95—110	3·5 ,,
70—75	1 ,,	110—115	nil
75—80	0 ,,	115—120	250 grams.
80—85	2 ,,		

The 90—95° *fraction consists mainly of a mixture of water and* *n*-butyl alcohol, which separates into two layers on cooling, the alcohol layer containing 19 per cent. of water and the aqueous layer 18 per cent. of alcohol.

The mixture boils at 91° and contains 35 per cent. of water.

In order to purify the *n*-butyl *alcohol thus obtained,* it was distilled over 1—2 per cent. of calcium, the fraction 116—117° being collected.

iso*Propyl Alcohol.*—In the identification of this alcohol in the oil, a few points of interest occurred.

After careful drying and distillation from solid sodium hydr-oxide, the alcohol was found to boil at 78—79°, and not at 83°, which is the value usually given.

The phenyl carbamate, after repeated recrystallisation from light petroleum, melted at 75—76° (Gumpert, *J. pr. Chem.*, 1885, [ii], **32**, 279, *gives* 90°, and Spica *and* de Varda, *Gazzetta*, 1887, **17**, 165, gave 42—43°). The phenylcarbamates of *n*-butyl and ethyl alcohols were found to melt at 61° and 51° respectively.

n-*Butaldehyde.*

(*a*) *By Direct Oxidation of* n-*Butyl Alcohol.*—The oxidation mixture used for the conversion of *iso*butyl alcohol into *iso*butaldehyde (Fossek, *Monatsh.*, 1881, **2**, 614) proved to be unsuitable for this preparation, and the following method of preparation was adopted.

Into 200 grams of *n*-butyl alcohol heated to 90—100°, a mixture of 200 grams of sodium dichromate, 180 grams of sulphuric acid, and 450 grams of water was slowly dropped at such a rate that there was continual ebullition. *n*-Butaldehyde, *n*-butyl alcohol, and *n*-butyl *n*-butyrate distilled over, and, after being dried, were separated by distillation. In three experiments, 58, 55, and 56 grams of *n*-butaldehyde were obtained, most of the alcohol being converted into *n*-butyl *n*-butyrate and tarry matter.

If the alcohol is dropped into the oxidation mixture, only traces of aldehyde are obtained.

Oxidation with ammonium persulphate, using cerium oxide as catalyst, gave only traces of *n*-butaldehyde.

(*b*) *Catalytic Method.*—The method employed was that of Bouveault (*Bull. Soc. chim.*, 1908, [iv], **3**, 118), in which carefully reduced copper hydroxide, suspended on copper gauze heated to 300°, is used as catalyst.

If care is taken, the catalyst does not deteriorate, although traces of *n*-butyric acid appear to be formed. The yield is theoretical,

and about 50—100 grams per hour can be obtained from a "catalyser" 45 cm. × 1·9 cm.

If the catalyst is heated to 400°, further dehydrogenation takes place, and some crotonaldehyde is obtained in addition to *n*-butaldehyde.

a-Ethyl-Δ^a-hexenealdehyde.

This was prepared by a modification of Raupenstrauch's method (*Monatsh.*, 1887, **8**, 108).

n-Butaldehyde (20 grams) and ether (10 c.c.) were mixed with a quantity of 10 per cent. aqueous potassium hydroxide, the whole was shaken for two hours, and allowed to remain for fifteen hours. The product was then washed with dilute sulphuric acid and water, dried, and distilled. On distillation, water was eliminated quantitatively from the aldol, giving the aldehyde boiling at 172—173°/760 mm.

The results with varying amounts of 10 per cent. potassium hydroxide solution were as follows, 20 grams of *n*-butaldehyde being used in each case:

Ten per cent. potassium hydroxide. c.c.	Product, b. p. 150—180°. Grams.	Yield. Per cent.
0·5	A few drops only	—
1·0	4	23
2·0	11	63
3·0	11·5	66
4·0	12·7	71
5·0	10·5	60

Other experiments, using 1 c.c. of the potassium hydroxide solution to 5 grams of *n*-butaldehyde, gave the following results:

Butaldehyde. Grams.	Yield. Per cent.
80	71·2
40	67·5
100	68·0

The *semicarbazone* melts at 132°.

In addition to a 70 per cent. yield of the "aldol," some of the *n*-butaldehyde is recovered unchanged, and some is converted into a substance boiling above 180°, which is probably identical with the unsaturated aldehyde, $C_{12}H_{22}O_2$, described by Gorhan (*Monatsh.*, 1905, **26**, 73).

a-Ethylhexyl Alcohol.

To 37 grams of *a*-ethyl-Δ^a-hexenealdehyde 16 grams of amalagamated aluminium and 200 c.c. of water were added, and

the mixture was allowed to remain for four days with occasional shaking. It was then distilled in a current of steam until no more oil passed over, and the distillate boiled under reflux for two hours with 5 grams of sodium hydroxide to remove any unreduced aldehyde as resin. The mixture was then distilled in a current of steam, and the alcohol extracted from the distillate with ether, the solution dried, evaporated, and distilled, the fractions 175—195° being collected; on redistillation, 10 grams of α-ethylhexyl alcohol boiling at 180—185° were obtained.

α-Ethylhexoic Acid.

The acid corresponding with the above alcohol was obtained as follows. Thirty grams of the aldehyde were mixed with the silver oxide, obtained by adding the theoretical quantity of barium hydroxide to 90 grams of silver nitrate. This mixture was treated with 600 c.c. of $N/2$-barium hydroxide solution, a few c.c. at a time, the whole being kept cold and vigorously shaken. It was then allowed to remain for twelve hours. Excess of barium hydroxide was removed by means of carbon dioxide, and the clear solution acidified with sulphuric acid. The free acid was extracted with ether, the solution dried, evaporated, and distilled, the fraction 165—175° being collected. The crude, unsaturated acid was heated for twelve hours on the water-bath with a large excess of zinc and sulphuric acid. The reduced acid was extracted with ether, and ultimately 15 grams of an acid boiling at 225° (the fraction 220—226° was collected) were obtained.

The amide melted at 101·5°, and this melting point was not changed when the substance was mixed with the amide of α-ethylhexoic acid synthesised from ethyl malonate (Raper, T., 1907, **91**, 1837).

Action of Alkali Metals and Alkali Hydroxides on n-*Butyl Alcohol.*

The similarity of the above α-ethylhexyl alcohol and that (b. p. 181°) obtained by Guerbet from butyl alcohol led to the investigation of the action of sodium and sodinm hydroxide on *n*-butyl alcohol.

Guerbet (*loc. cit.*) deduced his formula from the results of an analysis of the mixture of acids formed by the oxidation of the alcohol by means of a chromic acid mixture, and it was considered necessary to repeat his work.

The method adopted in all experiments was to dissolve the sodium in the butyl alcohol and heat the solution of sodium butoxide in butyl alcohol in a silver beaker in an electrically heated autoclave

at various temperatures and for varying lengths of time. The hydrogen was allowed to escape from a valve, the pressure in the autoclave being kept at 40—50 atmospheres.

After cooling, the product was treated with water, and the alcoholic layer separated and washed with water. The combined aqueous portions were saturated with common salt, and the alcohol separating was added to the main bulk.

After distillation in a current of steam to remove all alcohol, the aqueous part was acidified with sulphuric acid, the liberated acids were collected, and the aqueous layer was distilled in a current of steam to recover all acid.

The alcohol was dried by means of common salt, the water being separated as brine, and the acid with calcium chloride.

Typical results are given in the following table, 500 grams of *n*-butyl alcohol being used in each experiment.

Sodium. Per cent.	Conditions.	Hydrogen evolved. Litres.	Octyl alcohol. Grams.	*n*-Butyric acid. Grams.	Octoic acid. Grams.
5	To 275° and cooled	37·0	107	98	7
10	To 225° ,, ,,	45·6	124	157	6
10	200° for 20 hours	—	216	199	20
10	250° ,, 10 ,,	—	212	214	21
10	To 275° and cooled	88·2	206	201	28

When 15 per cent. of sodium was employed, practically the whole of the butyl alcohol was converted into *n*-butyric and octoic acids. In one case, nearly 300 grams of octoic acid were obtained.

These experiments show that the effect of an amount of sodium up to 10 per cent. has no effect on the relative quantities of octyl alcohol and butyric acid calculated on the weight of sodium used. Above 10 per cent., the amount of acid is increased at the expense of the octyl alcohol, octoic acid being formed.

The temperature at which the reaction is carried out is unimportant so long as the heating is sufficiently prolonged.

Calcium also brings about the condensation of butyl alcohol to octyl alcohol, but very little acid is formed; thus, when 100 grams of *n*-butyl alcohol were heated with 20 grams of calcium for ten hours at 235°, 20 grams of octyl alcohol and 4·6 grams of *n*-butyric acid were obtained.

The octoic acid (Found: C = 66·71; H = 11·04. Calc.: C = 66·60; H = 11·20 per cent.) and octyl alcohol (Found: C = 73·79; H = 13·49. Calc.: C = 73·76; H = 13·94 per cent.) have boiling points (225° and 181° respectively) almost identical with *a*-ethylhexoic acid and *a*-ethylhexyl alcohol, and since the acid is formed from the alcohol by simple oxidation, it must have a corresponding constitution. Its identity with *a*-ethylhexoic acid was proved

by the fact that mixtures of the amide with the amide of α-ethylhexoic acid (prepared as above and by Raper's method) melted at the same temperature as the latter, namely, 101·5°.

Octylene.—α-Ethylhexyl alcohol, when passed over aluminium oxide at 380—400°, loses water, giving an *octylene.* One hundred grams of the alcohol gave 71 grams of oil and 20 grams of water. The oil was fractionated as follows:

Up to 110°	9 grams.
110—125	53 ,,
Above 125	8 ,,

The pure octylene boils at 121°.

Dioctylene.—When the octylene is shaken with 80 per cent. sulphuric acid, a pleasant-smelling oil is formed, which boils at 245—250°. It is a hydrocarbon of the empirical formula C_8H_{14}, probably a *dioctylene.*

Fifty grams of the octylene, when shaken with 50 grams of sulphuric acid and 10 grams of water, gave, after washing with *potassium carbonate:*

Up to 120°	4·5 grams.
120—220	5 ,,
220—260	25 ,,
Above 260	5·5 ,,

Action of Sodium Hydroxide on n-*Butyl Alcohol.*

The reaction was carried out as in the preparation of α-ethylhexyl alcohol, sodium hydroxide being used in place of metallic sodium.

Typical experiments are given in the following table:

Sodium *hydroxide.* Grams.	*n*-Butyl *alcohol.* Grams.	*n*-Butyric *acid.* Grams.	α-Ethylhexoic *acid.* Grams.
150	500	233	5
250	760	414	10
400	760	700	25

The mixture was in each case heated at 275° for about three hours, the heating being stopped when no more hydrogen was evolved. In all cases, the unchanged alcohol was recovered, the loss varying from 1 to 5 per cent. of the whole. The method of working up was the same as that employed in the preparation of α-ethylhexyl alcohol. In addition to the production of *n*-butyric and α-ethylhexoic acids, about 1 per cent. of α-ethylhexyl alcohol was formed.

Action of Calcium Oxide and Hydroxide on n-*Butyl Alcohol.*

The amount of acid produced from *n*-butyl alcohol by the action of calcium is much less than that formed by sodium, and this fact leads to the conclusion that calcium hydroxide is much less active in the production of acid than sodium hydroxide.

Two experiments carried out with calcium oxide and hydroxide confirmed this.

Calcium Oxide.—One hundred grams of *n*-butyl alcohol and 40 grams of quicklime, when heated for eleven hours at 250—260°, gave, during the first hour, 800 c.c. of hydrogen, during the second hour 300 c.c., and after that none.

The products consisted of 6·5 grams of *n*-butyric acid and 14 grams of α-ethylhexyl alcohol, which on redistillation gave 12 grams of alcohol boiling at 180—185°. The yield of *n*-butyric acid was only 25 per cent. on the *n*-butyl alcohol attacked by the quicklime.

Calcium Hydroxide.—After ten hours' heating at 250—260°, 100 grams of *n*-butyl alcohol and 40 grams of slaked lime gave only 100 c.c. of hydrogen, 0·6 gram of *n*-butyric acid, and 1 gram of α-ethylhexyl alcohol.

Acetic Acid from Ethyl Alcohol.

Owing to the ease with which *n*-butyric acid can be obtained from *n*-butyl alcohol by heating with sodium hydroxide, an attempt was made to apply the reaction to the production of acetic acid from ethyl alcohol. Two preliminary experiments only were carried out, but these showed that the process could not be a commercial success.

Expt. 1.—Fifty grams of ethyl alcohol and 20 grams of sodium hydroxide were heated at 230—250° for three and a-half hours, the product being dissolved in water, acidified with sulphuric acid, and distilled to dryness under diminished pressure.

The acetic acid in the distillate, estimated volumetrically, was 4 grams, or 13 per cent. on the sodium hydroxide.

Expt. 2.—Sixty grams of ethyl alcohol and 20 grams of sodium hydroxide were heated for seventeen and a-half hours at 250—260°. The product was worked up as above, and 8 grams of acetic acid were obtained, that is, 26 per cent. on the sodium hydroxide.

Not only was the yield of acetic acid poor, but much of the alcohol was not recovered, owing to the formation of much resin. From this it seems probable that either acetaldehyde or a substance which readily gives this is formed as an intermediate product.

n-*Hexyl Alcohol and* n-*Hexoic Acid.*

The experiments on the production of hexyl alcohol and hexoic acid from a mixture of *n*-butyl and ethyl alcohols were not very successful, the yields being very poor.

The three following experiments may be quoted as typical of those carried out.

Expt. 1.—A solution of 50 grams of sodium in 250 grams of *n*-butyl alcohol and 200 grams of ethyl alcohol was heated in the autoclave to 275°, and then allowed to cool. The product was dissolved in water, the alcohols distilled in a current of steam, and salted out from the distillate by means of potassium carbonate. The acids were liberated from the aqueous portion by means of sulphuric acid, separated, dried, and distilled, acetic acid remaining in the aqueous portion. On redistillation, 45 grams of an acid boiling at 198—202° were obtained.

Expt. 2.—Seventy-five grams of sodium were dissolved in ethyl alcohol, and the excess of the latter was evaporated under diminished pressure. The sodium ethoxide was dissolved in 500 grams of *n*-butyl alcohol, and the solution treated as before, 75 grams of an acid boiling at 198—202° being obtained.

Expt. 3.—A solution of 70 grams of sodium in 450 grams of *n*-butyl alcohol and 140 grams of ethyl alcohol was heated at 275° and treated as in Expt. 1. From this, 82 grams of an acid boiling at 198—202° were obtained, and from the alcohol boiling at above 125°, in addition to α-ethylhexyl alcohol (b. p. 181°), an alcohol boiling at 166—168° was isolated. The corresponding acid, when purified, boiled at 199—200° and melted at 3°.

The amide melted at 97—98°, and a mixture of this with the amide of *n*-hexoic acid melted at 98—99°. The acid is therefore *n*-hexoic acid and the alcohol is *n*-hexyl alcohol.

Δ^{γ}-*Heptylene*-β-*one* (n-*Butylideneacetone*).

n-Butaldehyde and acetone in molecular proportions are shaken with 1—2 per cent. of solid sodium hydroxide; after a few minutes, the mixture emulsifies and becomes almost solid and very hot. The yield is not increased by cooling, but the amount of material of high boiling point is decreased. The temperature rises to 50—60°, and when it begins to fall the reaction is complete. The mixture is pale yellow, and, on cooling, water separates and the mixture becomes cloudy.

On distillation, in addition to butylideneacetone and unchanged materials, a small quantity of hydrocarbons (b. p. below 120°) is

btained, presumably formed by the dehydration of butylidene-cetone. The same hydrocarbons are apparently obtained by the action of aluminium oxide on a mixture of butaldehyde and acetone see below).

The results of experiments with 65 grams of *n*-butaldehyde, 50 grams of acetone, and 2 grams of sodium hydroxide are as follows:

Conditions.	Up to 140°. Unchanged. Grams.	140—180°. Butylidene-acetone. Grams.	Above 180°. Tar. Grams.
Shaken for 12 hours at 37° ...	22·0	30·0	27·0
,, ,, 12 ,, 15° ...	22·0	22·0	24·5
Shaken for 12 hours	19·0	18·0	34·0
Shaken in the cold	31·5	36·0	18·0
Shaken without cooling	28·0	34·5	23·0

The loss in all cases is due to acetone dissolved in the washing with water, so that the method of working up without allowing to remain gives not only a higher yield of butylideneacetone, but also less material of high boiling point, which may be regarded as loss.

No indication of mesityl oxide or phorone was obtained in the material of high boiling point. From the fraction 165—220°, α-ethyl-Δ^{α}-hexenealdehyde was isolated in appreciable quantities, but the main constituent of this fraction was butylideneacetone.

Δ^{γ}-Heptylene-β-one (*n-butylideneacetone*) is a colourless liquid which rapidly turns yellow on exposure to the air. The pure ketone boils at 157°, but on distillation always leaves some residue, which suggests that auto-condensation takes place, or that the compound absorbs water from the air, giving the "aldol," which decomposes to some extent on distillation, and is also readily oxidised by the air.

Ultimate analysis gives low results (compare Franke and Kohn, *Monatsh.*, 1899, **20**, 876, who found the same in the case of *iso*butylideneacetone). After very careful drying, treating with calcium chloride for two weeks, and distilling in a vacuum, the following result was obtained:

0·1102 gave 0·2957 CO_2 and 0·1007 H_2O. C = 73·18; H = 10·22.
$C_7H_{12}O$ requires C = 74·93; H = 10·79 per cent.

The *semicarbazone*, $C_8H_{15}ON_3$, is readily soluble in alcohol and melts at 118°.

On dehydration with 60 per cent. sulphuric acid (Kipping and Perkin, T., 1890, **57**, 13) or on heating with sodium hydrogen sulphate at 150°, butylideneacetone gives an oil with a terpene-like odour and much tar.

Action of Reduced Copper.—By passing butylideneacetone over

carefully reduced copper oxide heated to 700—800°, a small quantity of toluene was obtained, together with some phenolic substance, which appears to be a cresol, probably formed in the following manner:

$$\begin{matrix}Me\\O\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH{=}CH\\CH_3\cdot CH_2\end{matrix}\!>\!CH_2 \longrightarrow \begin{matrix}Me\\HO\end{matrix}\!>\!C\!<\!\begin{matrix}CH{=}CH\\CH_2\cdot CH_2\end{matrix}\!>\!CH_2.$$

This compound then loses four atoms of hydrogen, and the hydroxyl group migrates, giving a cresol. Most of the butylideneacetone, however, is converted into carbon and gaseous products. Experiments were carried out at various temperatures, but whenever toluene was obtained, the greater part of the ketone gave carbon and gases. At 600° a 5 per cent. yield of toluene was obtained.

Action of Aluminium Oxide on a Mixture of n-*Butaldehyde and Acetone.*

By passing butylideneacetone over aluminium oxide at 300°, it loses water, giving unsaturated hydrocarbons, which are apparently the same as those obtained in the preparation of the ketone by means of solid sodium hydroxide.

This led to the investigation of the action of aluminium oxide on a mixture of *n*-butaldehyde and acetone.

When a mixture of molecular proportions of *n*-butaldehyde and acetone is passed over aluminium oxide at 300—350°, water is lost and a certain amount of butylideneacetone is formed. This, however, seems to be an intermediate product, which on further dehydration gives two hydrocarbons, C_7H_{10}, possibly of the formulæ $CH_3\cdot CH_2\cdot CH_2\cdot CH{:}C{:}C{:}CH_2$ and

$$CH_3\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot C{:}CH.$$

One of these appears to boil at about 100°, and gives a precipitate with ammoniacal cuprous chloride. It is therefore an acetylenic hydrocarbon. The other boils at about 60—70°.

Only a few preliminary experiments have been made, but the optimum temperature appears to be about 325—350°. Above 400° charring takes place on the aluminium oxide, but at 350° the catalyst will apparently dehydrate an unlimited amount of butaldehyde and acetone.

Butylideneacetone only has been definitely proved to be present in the product.

The experiments which have been carried out with 50 grams of *n*-butaldehyde and 40 grams of acetone can be summarised as follows:

	i. Grams.	ii. Grams.	iii. Grams.
Oil	62·0	71	74
Water	16·5	13	9

Fractionation of the oil gave:

Up to 100°	24·0	38	41·5
100—125	2·0	3	4·0
125—145	2·5	3	4·5
145—170	18·0	12	12·0
170—200	3·0	3	3·0
Above 200	6·5	8	5·5

In this series of experiments, the more rapidly the materials were passed over the catalyst, the less water was produced and the more butylideneacetone (145—170°). This points definitely to the latter being an intermediate product in the formation of the hydrocarbons of low boiling point, and this is borne out by the results obtained on passing butylideneacetone over aluminium oxide, when water is lost. Thus, 42 grams of butylideneacetone yielded 32 grams of oil which, on fractionation, gave:

Up to 65°	1·0 gram.
65—140	5·5 grams.
140—170	18·0 ,,
Above 170	7·0 ,,

Action of Aluminium Oxide on a Mixture of n-*Butyl alcohol and Acetone.*

A mixture of 460 grams of acetone and 590 grams of *n*-butyl alcohol was passed over aluminium oxide at 300—350°.

The product consisted of 550 grams of oil and 238 grams of water, and much gas was evolved. Fractionation of the oil gave:

	Grams.		Grams.
Up to 55°	30	115—125°	73
55— 65	126	125—145	6
65— 75	24	145—155	48
75— 85	22	155—180	6
85— 95	18	180—210	35
95—105	21	Above 210	53
105—115	61		

From this the following products have been isolated:

(i) A *hydrocarbon*, boiling at 76—78°, probably C_7H_{14} from (iv) by dehydration.

(ii) A *heptadiene*, boiling at 94—96°:

0·1273 gave 0·4088 CO_2 and 0·1538 H_2O. C=87·57; H=13·51.

C_7H_{12} requires C=87·41; H=12·59 per cent.

This is probably formed by the dehydration of methyl amyl ketone (iii).

(iii) Methyl amyl ketone (b. p. 148—150°), which was isolated by means of its sodium hydrogen sulphite compound. The melting point of its semicarbazone (120°) was not altered by admixture with a specimen from another source.

(iv) An unsaturated *alcohol*, boiling at 150°, probably isomeric with methyl amyl ketone.

Substances boiling at 70—80°/13 mm. and 100—110°/13 mm., together with traces of *n*-butaldehyde and *iso*propyl alcohol, were also isolated.

The chief products were methyl amyl ketone and the heptadiene.

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XLII.—*An Investigation of the Resin from Species of Xanthorrhoea not previously examined.*

By EDWARD HENRY RENNIE, WILLIAM TERNENT COOKE, and HEDLEY HERBERT FINLAYSON.

XANTHORRHŒA resin has been the subject of many investigations, but unfortunately the authors of these investigations do not always seem to have been certain as to the species from which the resin had been derived. For the most part, the resin examined appears to have been obtained from New South Wales, and is described as "red" or "yellow." Tschirch in his "Harze und Harzbehälter" says: "Was die Abstammung der Acaroide betrifft, so ist dieselbe noch nicht sichergestellt. Für das gelbe wird *X. hastilis*, für das rothe meist *X. australis* angegeben." In the most recent examination made at the Imperial Institute, no reference is made to species, but the material used is described as "a commercial sample of red Xanthorrhœa resin."

The two species above referred to are not known in South Australia, and all the material used by us was obtained either from Kangaroo Island (South Australia) or West Australia. So far as the Kangaroo Island resin is concerned, we have again red and yellow varieties. The yellow has, so far as can be gathered from specimens of foliage, been obtained from *X. Tateana*, but, according to Mr. Harrison, of Kingscote, only about 1 per cent. of the trees yield the yellow resin. The origin of the red is still

uncertain. A specimen of foliage was submitted to Prof. Osborn of this University, who states that it would require investigation by a specialist on the spot to determine whether the leaves belong to a different species (from that which yields the yellow), or a variety, or whether age and environment may account for the differences in the leaves.

Those chemists who have published results of their work on the "red" and "yellow" resins agree substantially as to the products so far obtained, but some have found substances not noticed by others. As our work is concerned with material from species not, so far as we are aware, yet examined, it will suffice merely to mention the principal constituents recorded in resins from other species. Those are, briefly:

(1) *Acids*, either free or partly in the form of *esters*.—Benzoic, cinnamic, *p*-coumaric.

(2) *Aldehydes*.—Vanillin, *p*-hydroxybenzaldehyde.

(3) *Products of Oxidation by Alkaline Permanganate, Chromic Acid, etc.*—Acetic and oxalic acids, or insoluble chromium compounds.

(4) *Products of Fusion with Potassium Hydroxide.*—Resorcinol, *p*-hydroxybenzoic acid, carbonic acid.

(5) *Products of Action of Nitric Acid.*—Picric acid, *p*-nitrophenol, acetic acid.

(6) *Products of Distillation with Zinc Dust in the Presence of Hydrogen.*—Benzene, toluene, naphthalene.

(7) *Products of Destructive Distillation.*—Phenol, styrene, and tarry matters.

(8) A residue obtained by acidification of an alkaline solution consisting of a complex substance, which has been named a "resinotannol."

A. *Examination of the "Red" Resin.*

The resin used in the following experiments was carefully picked out and freed, as far as possible, from fragments of leaves, the quantity of which was quite insignificant.

Action of Nitric Acid.

Picric acid was obtained in quantity, and small quantities of another nitro-compound, which was not identified. Oxalic acid was also obtained.

Fusion with Sodium Hydroxide and Examination of the Product for Volatile Acids.

About 500 grams of the resin in 50-gram lots were fused gently for several hours with an equal weight of sodium hydroxide, a little water having been added. The fusion was acidified with sulphuric acid, distilled, and the distillate neutralised with sodium carbonate and evaporated to dryness. The greater part of the residue was added to a cold mixture of alcohol and concentrated sulphuric acid, frequently shaken, and allowed to remain overnight. The liquid was then gently distilled, and the distillate shaken several times with a saturated aqueous solution of potassium carbonate, the layer of ester run off, dried with potassium carbonate, and fractionated. The greater part of the distillate (apart from ether, due to the interaction of the alcohol and sulphuric acid) was found to be ethyl acetate, but there was also present a small fraction which had an odour like that of ethyl butyrate, and, on hydrolysis and acidification, gave the unmistakable odour of butyric acid. The total yield of esters was about 8 per cent. of the resin taken.

Oxidation with Alkaline Permanganate.

Twenty grams of the resin were boiled with alkaline permanganate (10 grams of $KMnO_4$ in 200 c.c. of solution) for half an hour, the solution then being acidified with sulphuric acid and distilled in a current of steam. Only traces of acid (acetic?) were present, with a minute quantity of a fragrant oil. The residue from the steam distillation was collected, washed, redissolved in sodium hydroxide solution, a further 10 grams of potassium permanganate added, and distilled. The distillate was neutral. On repeating the process, the resin was ultimately broken up, and nothing but carbonic acid could be recognised in the final product.

Examination for Acids either Present in the Free State or in the Form of Esters.

A large quantity of the resin (680 grams) was dissolved by the aid of excess of sodium hydroxide in about 2 litres of water, and the solution distilled in a current of steam for about twelve hours. The residue was just acidified with sulphuric acid, the solution filtered, and concentrated until a quantity of sodium sulphate crystallised out, the crystals (which were mixed with a crystalline organic substance) were warmed with alcohol, the latter was distilled off, and the tarry residue, as well as the acid solution, ex-

hausted with ether. The residue, after distillation of the ether, partly solidified on keeping, but contained some tarry matter, which, after considerable difficulty, was removed by exhaustion with boiling water and repeated treatment with animal charcoal. Ultimately, a nearly colourless, crystalline mass was obtained, and this was separated by means of chloroform into two substances, which, on examination, proved to be *p*-coumaric acid and *p*-hydroxybenzaldehyde. It seems scarcely necessary to go into details of the identification of these substances, repeatedly recognised as they have been by others as present in other varieties of Xanthorrhœa resin; suffice it to say that the former was fully identified by combustion, melting point, and other characteristics, the latter by methylation, conversion into anisaldehyde, and oxidation of the latter to anisic acid. The total yield of the two products (purified) was about 4·5 per cent., but it must be noted (a fact of which we were not at the time aware) that *p*-coumaric acid is slowly decomposed on boiling with dilute sulphuric acid. Hence the amount of this acid obtained in the way described above is no doubt considerably below that actually present. It was not thought necessary to make a careful search for other acids or aldehydes such as benzoic and cinnamic acids and vanillin, which have been found by other observers, but it is worth mentioning that, on acidification of the alkaline solution of the resin after steam distillation, for the purpose of extraction of the above-mentioned substances, a vanillin-like odour was often noticed.

Products obtained by Steam Distillation of a Strongly Alkaline Solution.

In the experiment above described, it was noticed that an appreciable quantity of a fragrant oil was obtained in the distillate. On shaking the distillate (6 litres) with ether and evaporating off the latter, about 1·5 grams of a fragrant oil remained, which, on keeping, solidified to a pale brown, crystalline solid. In order to examine this more thoroughly, several lots, of 1 kilogram each of the resin, were dissolved in alkali (about 200 grams of sodium hydroxide and 2 litres of water to each kilogram), and steam distillation was continued in each case until about 12 litres of distillate were collected and practically no more oil passed over. The distillates were then exhausted with benzene and the latter distilled off. From each such distillation, from 3·55 to 3·65 grams of residual oil were obtained, which, on keeping, always solidified. The total amount of material was then dissolved in alcohol, the solution filtered from a minute amount of insoluble matter, and

the material allowed to crystallise. Two recrystallisations brought the melting point to 49°, at which point it remained constant. The crystals were stout, well-developed needles, almost colourless, and had a sweet odour. (This fragrance was subsequently found to be due to a minute quantity of a fragrant oil, which was not present in sufficient quantity for identification, and adhered persistently. The crystals, when afterwards thoroughly purified, were found to have only a slight, somewhat phenolic odour.) They were freely soluble in ether, benzene, acetic acid, and most other organic solvents, very sparingly so in cold water, more freely in hot, readily soluble in solutions of alkali hydroxides, but insoluble in solutions of the alkaline carbonates or ammonia (Found: C = 64·78, 64·71; H = 5·99, 5·78. M.W. by cryoscopic method in benzene, 161. $C_9H_{10}O_3$ requires C = 65·06; H = 6·02 per cent. M.W. = 166).

On treatment with bromine in carbon tetrachloride solution, it yielded a crystalline bromo-derivative, and on acetylation an acetyl derivative melting at 44—45°. The hydrazone was also obtained. These facts agree with the data for paeonol, a product obtained from *Paeonia Moutan* in Japan, and used medicinally in that country. Its constitution has been proved to be that of 2-hydroxy-4-methoxyacetophenone, $CH_3 \cdot CO \cdot C_6H_3(OH) \cdot OMe$ (Nagai, *Ber.*, 1891, **24**, 2847; Tahara, *ibid.*, 2459).

The mother liquor, after separation of the paeonol, contained apparently nothing but a small quantity of the fragrant oil already referred to, the quantity of which was too small for examination.

Nitropaeonol.

For reasons which will appear in the sequel, it became desirable to prepare a nitropaeonol. Ten grams of paeonol in 30 c.c. of glacial acetic acid were mixed with 5 c.c. of nitric acid (D 1·41). After a few minutes, a characteristic, blue colour appeared, changing in the course of some hours to blood-red. For twelve hours after no further change took place, but on adding a further 10 c.c. of nitric acid, the mixture became warm, and, after a few minutes, deposited a crop of crystals, nitrous fumes being evolved in quantity and the red colour persisting. After remaining for some days, the liquid was diluted with its own volume of water, the crystalline deposit collected, washed, and repeatedly crystallised from hot alcohol until almost colourless. It consisted of long, straw-coloured needles melting at 153° (Adams, *J. Amer. Chem. Soc.*, 1919, **41**, 247, gives 155°) (Found: N = 6·56. $C_6H_9O_5N$ requires N = 6·63 per cent.). On reduction with tin and hydrochloric acid, removal of the tin by means of hydrogen sulphide, and concentration of the

red solution, the hydrochloride of the amino-compound rated out as a mass of needles, which were permanent in air were not further examined.

Examination of Yellow Resin of X. Tateana. *Isolation of a New Substance,* $C_9H_{10}O_4$.

The yellow resin differs in other respects than in its colour from red variety. It shows a marked tendency to accumulate in nps and tears varying in colour from pale amber to a muddy own, but it is always pure yellow when powdered. It is noticely less brittle than the red, becomes soft if placed in the mouth, d when boiled with water becomes a mobile liquid. It dissolves alkali hydroxides, yielding in moderate concentrations an orange lution, from which acids precipitate the resin as a dull, mustard-loured powder. Steam distillation was resorted to under contions exactly similar to those already described in the case of the d material, with the exception that the distillation was much ore prolonged, being continued in some cases until 150 to 160 tres of distillate had been collected, the reason being that apprecible quantities of oily matter continued to pass over for long periods f time. The oil obtained in this way gradually solidified on keepng. That in the earlier part of the distillation was very like paeonol, but later on quantities of solid matter quite different from paeonol made their appearance. The whole of these substances was extracted from the distillate by shaking with benzene. The total product after the evaporation of the benzene averaged, in several distillations, about 5 per cent. of the weight of material, a very much larger quantity than in the case of the red resin. Obviously there were two substances here present, which could be partly separated by collecting separately the earlier and later portions of the distillate. The earlier portions consisted practically entirely of paeonol, with a small quantity of the same fragrant oil noted in the case of the red resin. The later portions were recrystallised from dilute alcohol until a constant melting point, 79°, was reached. In subsequent experiments, the whole of both substances was extracted with benzene, and, after removal of the latter, the two were separated by fractional distillation under 20 mm. pressure. At this pressure, the paeonol boiled at 158° and the other substance at 185°. Of the total, about 60 per cent. was paeonol, and the remainder, except for a trace of some material of higher boiling point, the second substance. The substance obtained in this way was quite colourless, practically insoluble in cold or hot water, and readily soluble in alkali hydroxides or in

the ordinary organic solvents. Like paeonol, it gives a claret colour with ferric chloride. The colour reactions with nitric acid are very similar to those given by paeonol, but more marked. In cold concentrated nitric acid, an intense blue colour is immediately developed, which, on keeping, and particularly on warming, changes to a blood-red, which is not discharged by continued boiling with concentrated nitric acid. On diluting the red solution and rendering alkaline with sodium hydroxide, a dark green colour is developed, which, however, is somewhat fugitive.

Found: C=59·47, 59·78; H=5·70; 5·23.

$C_9H_{10}O_4$ requires C=59·34; H=5·49 per cent.

A molecular-weight determination by the cryoscopic method in benzene gave 178, the theory for $C_9H_{10}O_4$ being 182.

Oxidation.—The above figures, coupled with the general behaviour of the substance, in particular the close resemblance of its colour reactions to those of paeonol, suggested the probability that we were here dealing with an hydroxypaeonol. To decide this point, the following experiments were undertaken. A small quantity, 0·532 gram, was boiled in a small flask attached to a reflux condenser with a mixture of potassium chromate and 15 per cent. sulphuric acid, the former being added cautiously until the solution was permanently yellow. The mixture was then distilled almost to dryness, water added, and the boiling resumed until acid ceased to pass over. The distillate was redistilled, excess of barium carbonate added, the solution evaporated to dryness, the residue redissolved, and the solution filtered and finally evaporated to dryness in a tared platinum dish. The barium salt so obtained, after drying at 100°, weighed 0·2979 gram, and its reactions were those of barium acetate (0·23 gave 0·206 $BaSO_4$, whilst barium acetate requires $BaSO_4$=0·21). An hydroxypaeonol on oxidation should yield acetic acid.

Oxime.—To a solution of 4 grams of sodium hydroxide in 8 c.c. of water was added slowly, with cooling, a solution of 6 grams of the original substance and 2·5 grams of hydroxylamine hydrochloride in a mixture of 80 c.c. of alcohol and 20 c.c. of ether. After remaining for twelve hours, the red solution was heated under reflux for two to three hours, the excess of alcohol and ether distilled off, and the residue poured into water and acidified. The crude oxime was repeatedly crystallised from dilute alcohol until a constant melting point was obtained. The purified compound crystallised from alcohol in transparent plates, and from the dilute solvent as a grey sand. The air-dried substance, when slowly heated, sintered together at 100° and melted and decomposed at 107°, but this was found to contain water, the loss at 100° amount-

to 8·44 per cent. (theory for $1H_2O = 8·37$ per cent.). Appar-y hydrolysis takes place on drying, with loss of hydroxylamine, mations of nitrogen always giving low results. There could be doubt, however, as to the oximic character of the compound, the original substance could readily be obtained by hydrolysis, lroxylamine being easily recognised in the solution.

Iethylation to a Dimethyl Ether.—Six grams of methyl sulphate re added to a warm paste of 5 grams of the compound $C_9H_{10}O_4$, rams of sodium hydroxide, and 10 c.c. of water. The mixture ame very hot, and was allowed to remain for twelve hours. The ss was then dissolved in the least possible quantity of alcohol, d the solution poured into an excess of sodium hydroxide solu-n. The precipitated ether was collected, washed, and recrystal-ed three times from dilute alcohol, when the melting point came constant at 102—103° (Tutin and Caton, T., 1910, **97**, 67, give 99—100° as the melting point of 2:4:6-trimethoxyaceto-ienone). The ether so obtained was insoluble in alkali, and gave o coloration with ferric chloride. A blue colour with nitric acid eveloped very slowly (Found: C=62·44, 62·35; H=6·69, 6·60. I.W.=205. $C_{11}H_{14}O_4$ requires C=62·85; H=6·65 per cent. I.W.=210). These figures prove the existence of two hydroxyl roups in the compound $C_9H_{10}O_4$. On fusion with potassium hydr-xide, a little water at temperatures ranging from 120° to 230°, cidification of the product, and repeated extraction with ether, a rystalline substance was obtained which, after purification, was ompletely identified by its sweet taste, bluish-violet colour with ferric chloride, colour reaction with pine wood moistened with hydrochloric acid, and analysis as phloroglucinol.

The above experiments conclusively prove that the substance, $C_9H_{10}O_4$, is a monomethyl ether of 2:4:6-trihydroxyacetophenone. The position of the methoxy-group remains to be determined. The close association of this compound with paeonol, and the similarity of its reactions to those of paeonol, render it probable that the methoxy-group is in the para-position, but so far we have been unsuccessful in definitely proving this point. It was thought possible that nitration of paeonol, reduction of the nitro- to the amino-compound, diazotisation, and decomposition by water might yield an hydroxypaeonol which would be either identical with or different from the compound under consideration. The nitration and reduction of the nitro-compound have already been described. On diazotisation of the latter, however, and boiling with water, coupling or some other change apparently takes place, and a deep brown substance is obtained, which has not been further examined.

Examination for Acids, Free or Combined.

The alkaline solution, after steam distillation, was acidified and examined exactly as described in the case of the red resin, and again *p*-coumaric acid and *p*-hydroxybenzaldehyde were identified in considerable quantity.

C. *Examination of* X. Preissii.

We are indebted to Mr. Lane-Poole, Conservator of Forests in W. Australia, for a supply of this resin, which we have examined by the same method of steam distillation, as already described. Since the work was completed, a letter was received from the Government Chemical Laboratory, W.A., enclosing a report from Mr. D. A. Herebert, the economic botanist and pathologist, in which it is stated that a new species of *Xanthorrhoea* has been discovered which is very like *Preissii*, the resin of which, however, is black, that of *Preissii* being red. The samples of resin forwarded to us by Mr. Lane-Poole were all red, however, and there was no evidence of the presence of any of the black variety. A small quantity of the black variety may have been present and escaped notice, but not sufficient, we think, appreciably to vitiate the results of our work.

Products of Steam Distillation.

On distillation with steam in the way already described, a yellow oil was obtained much more fragrant than that produced from the other species above referred to, the total yield being a little more than 1 per cent. The first portious of oil passed over very rapidly, but even after long and tedious distillation (160 litres of distillate from 3 kilograms) the distillate was still turbid. This is in sharp contrast with the result obtained with *X. Tateana*, the distillate in the latter case being quite clear when the distillation was stopped. As in previous cases, the distillate was exhausted by shaking with benzene, and the latter distilled off. The residue was then carefully fractionated under 20 mm. pressure, and ultimately five fractions were collected, namely, 110—155°, 155—165°, 165—185°, 185—200°, and 200—210°, leaving a small quantity of a somewhat viscous, uncrystallisable material in the flask. Fraction 2 (155—165°) proved to be almost entirely paeonol. Fraction 3 was chiefly paeonol with a small quantity of an oil which did not crystallise. Fraction 4 remained liquid for some weeks, but

lly deposited crystals which, on washing with small quantities alcohol and recrystallisation, melted at 79°, and proved to be hydroxypaeonol already described.

Isolation of a Compound, $C_{13}H_{12}O_2$.

Fraction 5 was solid, and was recrystallised from alcohol until e melting point was constant at 69·5°.

Found: C = 78·24; H = 6·44.

$C_{13}H_{12}O_2$ requires C = 78·00; H = 6·00 per cent.

The figures agree better with the formula $C_{13}H_{12}O_2$ than with $_{13}H_{14}O_2$.

A molecular-weight determination by the cryoscopic method in enzene gave 194 ($C_{13}H_{12}O_2$ requires 200). The substance is practically insoluble in cold or hot water and in alkali hydroxides, but issolved easily in the ordinary organic solvents. Its alcoholic olution gives no coloration with ferric chloride. It is not acted on by acetic anhydride. All attempts to form from it an oxime or hydrazone failed. On the other hand, it was found to contain one methoxy-group, an estimation by the ordinary method giving OMe = 15·1, whilst $C_{12}H_9O{\cdot}OMe$ requires OMe = 15·5 per cent. With cold concentrated nitric acid, a black, tarry material was at once formed, with evolution of nitrous fumes, but on slow evaporation an orange substance remained, from which nothing definite has so far been obtained. Potassium dichromate and dilute sulphuric acid attack it very slowly, and again no definite product could be obtained. It dissolved gradually in cold concentrated sulphuric acid, forming a pale yellow solution, from which, on dilution, it was deposited apparently unchanged. With hot concentrated sulphuric acid, dirty green solutions were obtained, which at the fuming point assumed a rich purple tint, but no charring took place, and the solution, on pouring into water, yielded a flocculent, red precipitate. These facts appear to indicate that the compound is a methoxydiphenyl ether, and its general characters are in harmony with that supposition. Derivatives of diphenyl ether, with few exceptions, appear to have been little studied, and all seem to be characterised by considerable stability.

An attempt was made to synthesise *p*-methoxydiphenyl ether by the preparation of *p*-nitrodiphenyl ether, its reduction to the amino-compound, the diazotisation of the latter, the decomposition of the diazo-compound with water, and methylation of the product. The first stage was carried out successively by Haeussermann and Teichmann's method (*Ber.*, 1896, **29**, 1446). A mixture of

potassium phenoxide, excess of phenol, and *p*-chloronitrobenzene was heated for two to three hours in an oil-bath to 150—190° in a flask with reflux condenser, a stream of hydrogen being passed through the apparatus. On cooling the mass, water was added, and the alkaline solution extracted with ether. The residue, after evaporation of the latter, was distilled under 20 mm. pressure, and practically pure *p*-nitrodiphenyl ether obtained. The reduction of the nitro-compound was effected without difficulty, and the amino-compound obtained in white crystals. On diazotisation and boiling with water, a tarry mass was produced, which was extracted with ether, and the residue, on evaporation of the latter, methylated by methyl sulphate in alkaline solution. The material which separated was small in quantity, and on distillation yielded only a small quantity of liquid boiling at 170°/20 mm., which was not the desired compound. We hope to make further experiments in the future.

Isolation of Citronellol.

Fraction 1 (110—155°) of the oil from *X. Preissii* was carefully fractionated, with the result that a large proportion of it was obtained as a fragrant oil boiling at 118—120°/20 mm. with smaller quantities of fragrant substances of lower boiling point. It was colourless, somewhat viscid, and had a distinct rose-like odour, quite different from that of geraniol, which it was at first suspected to be. To ascertain whether any esters were present, the ester value was determined by boiling with alcoholic potassium hydroxide and titrating with sulphuric acid, but was found to be only 14. On acetylation, however, the ester value rose to 280, which corresponds with 96—98 per cent. of acetates derived from the possible alcohols $C_{10}H_{16}O$, $C_{10}H_{18}O$, or $C_{10}H_{20}O$. In order further to purify the oil, it was heated under reflux with fairly concentrated alcoholic potassium hydroxide, a treatment which had no effect on the odour or boiling point (Found: C=76·56; H=13·14. $C_{10}H_{20}O$ requires C=76·92; H=12·82 per cent.).

This alcohol proved to be optically active, a solution of 2·369 grams in 20 grams of benzene giving a rotation of −1·1° at 13° in a 2-dcm. tube. Hence $[\alpha]_D^{13}$ −5·27°, which is not far from the value −4·20° ascribed to *l*-citronellol. The identity with citronellal was finally determined by conversion into the hydrogen phthalic ester. To the above solution in benzene were added 2·5 grams of finely powdered phthalic anhydride, and the mixture was boiled under reflux for five hours. The benzene having been distilled off, a viscid oil remained which, on keeping overnight, partly solidified. On washing with light petroleum, the oil was separated

a the crystals, which proved to be unchanged phthalic ydride. From the petroleum washings the ester was recovered distillation of the solvent as a colourless, permanent oil without ur. It was completely soluble in potassium hydroxide. On ling an almost neutral solution of the hydrogen phthalic ester sodium carbonate to a fairly concentrated solution of silver rate, a white, curdy, silver salt was precipitated, which was tained in small rosettes of very fine needles by crystallisation om boiling methyl alcohol. After drying in a vacuum, these elted at 125°, and on ignition gave Ag=25·89 (Calc.: Ag=26·23 er cent.). These facts leave no doubt as to the identity of the l with citronellol.

It is noteworthy that the higher fractions obtained by the dis- illation of the crude oil had an odour of mint. This suggests the resence of *iso*pulegol, which would probably be formed during the epeated fractionation of the crude oil if it contained some itronellal, which is quite probable (compare Schimmel's *Reports*, April, 1909, p. 94).

Examination for Acids.

An examination of *X. Preissii* for acids led to the identification of *p*-coumaric acid, but *p*-hydroxybenzaldehyde was not detected, although it may have been present in small quantity.

Residues after Steam Distillation and Acidification.

The solids obtained by acidifying the alkaline solutions after steam distillation have been carefully washed and preserved. We hope soon to investigate them more thoroughly.

Summary.

(1) The *Xanthorrhoea* resins from Kangaroo Island and W. Australia, in common with other species examined by various chemists, contain *p*-coumaric acid, either in the free state or in the form of an ester, and *p*-hydroxybenzaldehyde.

(2) By steam distillation from a strongly alkaline solution, the following substances not hitherto found in Xanthorrhœa resin have been obtained:

A. *Red Resin from Kangaroo Island* (Sp. ?).—(*a*) A small quantity of fragrant liquid of vanillin-like odour; (*b*) paeonol (2-hydroxy-4-methoxyacetophenone); (*c*) traces of material of higher boiling point.

B. *Yellow Resin from* X. Tateana (*Kangaroo Island*).—(*a*) A small quantity of fragrant liquid of vanillin-like odour; (*b*) paeonal in much larger quantity than in the red resin; (*c*) hydroxypaeonol in quantity about two-thirds of that of the paeonol; (*d*) a small quantity of material of higher boiling point.

C. *Red Resin from* X. Preissii (*W. Australia*).—(*a*) A small quantity of fragrant liquid not identified; (*b*) *l*-citronellol; (*c*) paeonol; (*d*) hydroxypaeonol; (*e*) a compound, possibly methoxydiphenyl ether; (*f*) a small quantity of so far uncrystallised material of very high boiling point.

This investigation has been carried out by us as a special committee appointed for the purpose by the Australian Commonwealth Institute of Science and Industry.

We have to thank Mr. W. W. Hurst, originally a member of the Committee, for help rendered in the earlier part of the work, and Mr. F. L. Winzor for great assistance in the latter portion.

THE UNIVERSITY,
ADELAIDE. [*Received, February 20th,* 1920.]

XLIII.—*Coagulation of Metal Sulphide Hydrosols. Part II. Influence of Temperature on the Rate of Coagulation of Arsenious Sulphide Hydrosols.*

By JÑANENDRA NATH MUKHERJEE.

CERTAIN observations of Linder and Picton (T., 1905, **87**, 1906) show that temperature has a very marked and anomalous effect on the coagulating power of an electrolyte. It is similar to the irregular effect of dissolved hydrogen sulphide observed by the author and Sen (T., 1919, **115**, 462). The effect of temperature on the velocity of coagulation is undoubtedly of importance for the elucidation of the mechanism of coagulation, but, unfortunately, little has been done on the subject. In their work, Linder and Picton did not attempt any study of the effect of temperature on the rate of coagulation. Moreover, as they employed an unsound method of measuring the coagulating power, their results are inaccurate, as would appear from the following quotation: "The required concentration of the salt is generally diminished by rise of temperature. Thus, at 15° and 70°, the volume of *N*/25-calcium chloride was 3·85 and 2·30 c.c. respectively, the latter representing

a decrease of 40 per cent. Similar results were obtained with calcium nitrate, hydrochloric acid, strontium nitrate, and aluminium sulphate. On the other hand, the reverse effect was noticed with ammonium chloride, sulphuric acid, and ammonium sulphate. Thus, at 13° and 61°, the volume of $N/2$-ammonium chloride was 3·47 and 4·44 c.c. respectively, the latter representing an increase of 28 per cent." In his experiments, Paine (*Proc. Camb. Phil. Soc.*, 1912, **16**, 430) remarks: "There is no very marked change (but slight increase) in the rate of coagulation on raising the temperature to 100°." He warmed his sols to hasten the separation of what he called "the coagulated portion."

EXPERIMENTAL.

The procedure described in the former paper (*loc. cit.*) was employed. Colloidal solutions like those studied are always "ageing," and the observations should always be simultaneous. The data only show the comparative effects of the particular condition that is changed. The method used herein is sufficiently accurate for the purpose in view, and unless the process of "ageing" has been fully accounted for, there is not much need to make it more accurate. However, the method can easily be made instrumental and as accurate as desirable, and the author is at present engaged in this with a view to elucidate the stability relations of these sols.

In the case of dilute sols, the mixture of electrolyte and sol was continuously kept stirred by jerking the tube with the hand. This gives a sharp change for the first appearance of visible particles throughout the liquid. For sols rich in sulphide, this was not done, for reasons given before (*J. Amer. Chem. Soc.*, 1915, **37**, 2024), and the times for perceptible change and for certain definite degree of opacity were noted.

Five c.c. of electrolyte and 5 c.c. of sol were immersed in a beaker containing water, which was suspended inside a thermostat. About one-fourth of the length of the tubes remained above the surface of the water. In order to minimise the errors in measuring the volumes, the same two pipettes were always used, one for the sol and the other for the electrolyte, thus keeping the relative volumes constant. This is a necessary precaution to obtain trustworthy agreement between different readings. After the liquids in the tubes had attained the temperature of the bath (about an hour), they were withdrawn, and the electrolyte was added to the sol. The test-tube containing the liquid was then again immersed in the water of the beaker. The whole process does not take more than half a minute. The tubes were taken up from time to time and observed.

Different preparations of the sol were always tried, and at least two readings taken. At least four different concentrations of the same electrolyte were used. The results are concordant. The electrolytes studied were hydrochloric acid, potassium chloride, sodium chloride, lithium chloride, potassium sulphate, potassium nitrate, sulphuric acid, barium chloride, calcium chloride, calcium bromide, strontium chloride, magnesium chloride, magnesium sulphate, aluminium sulphate, and thorium nitrate. The salts were purified samples of the best materials available.

It is possible that, on heating, the sol undergoes an irreversible change. In order to test this, samples of sol and electrolyte were heated in the bath along with the others, for the same interval of time, and were then cooled and the times for the respective changes noted. There was no perceptible difference between these samples and others which were not so heated, showing that there is no irreversible change under these conditions within the limits of experimental error. It is necessary to treat the electrolyte similarly to see whether there has been any appreciable change in its concentration due to loss by evaporation. In general, the observations were finished within five hours, and in some cases within two hours, after immersing the tubes in the bath. It is interesting to note in this connexion that Kruyt and Spek (*Kolloid Zeitsch.*, 1919, **25**, 1) find that on long-continued boiling of arsenious sulphide sols at 100—105°, the size of the particles decreases markedly. In the present instance, the temperature effect must be explained in terms of a reversible change in the quality of the sol in case it undergoes any such change.

The results show an irregular effect analogous to that noticed by the author and Sen with dissolved hydrogen sulphide (*loc. cit.*). The electrolytes can be broadly classified in groups determined by their valency. Within each group the results are perfectly regular, and, so far as can be judged, the different cations in the same group are affected in an equal degree by any given variation in the conditions of experiment. Contrary to the observation of Linder and Picton quoted above, both hydrochloric acid and sulphuric acid effect a diminution in stability at higher temperatures. In this respect, the hydrogen ion behaves in a different way from the rest of the univalent cations.

With cations of the barium group there is in each case a diminution in stability with rise in temperature. The experiments with aluminium and thorium salts will be dealt with separately, because of certain striking peculiarities. In the following table, a few of the data with uni- and bi-valent cations are recorded for comparison. The times given denote the interval, after mixing the

sol and the electrolyte, necessary to produce a definite change in the sol. The concentrations refer to "end" concentrations. As stated before, the change in the sol which is observed varies with the nature of the sol. The times are strictly comparative only for a particular sample observed at different temperatures. The observations at different temperatures were made side by side and always on the same day. The sulphide contents of the different sols are given below. Sol *A* contains 1·925 millimoles of arsenious sulphide. Sols *B*, *C*, and *F* have the same sulphide content, namely, 14·23 millimoles per litre. Sols *D*, *E*, and *I* contain 3·5575 millimoles of sulphide per litre, but sol *E* contains an equal amount of arsenious oxide in excess. Sols *H* and *J* each contain 4·8 millimoles per litre. In comparing the different sols, it *should be remembered that the behaviour of a sol is not determined* by its sulphide content alone.

TABLE I.

Electrolyte.	Concentration.	Sol used.	Times required at different temperatures	
			25°.	45°.
1. Potassium chloride	$17N/200$	*A*.	4 mins.	38 mins.
2. ,, ,,	$N/20$	*B*	14 ,,	38 ,,
3. ,, ,,	$N/18$	*B*.	4 ,,	10 ,,
4. ,, nitrate	$N/20$	*C*.	1 hr. 51 mins. (14·5°)	3 hrs. 39 mins.
			14·5°.	45°.
4. Potassium sulphate	$N/7$	*D*.	3½ mins.	4 hrs. 2 mins.
5. ,, ,,	$N/7$	*E*.	1 min.	20 mins.
6. Sodium chloride...	$3N/40$	*F*.	10 mins.	4 hrs. 42 mins.
7. Hydrochloric acid	$0{\cdot}07385N$	*D*.	5 ,,	about 1 min.
8. ,, ,,	$0{\cdot}07385N$	*E*.	4 ,,	,, 1½ mins.
9. Sulphuric acid ...	$0{\cdot}08438N$	*E*.	40 ,,	23 mins.
10. Hydrochloric acid	$0{\cdot}0733N$	*E*.	11 ,,	3 ,,
			28°	65°.
11. Barium chloride ...	$N/800$	*H*.	5 mins.	1 min.
12. Calcium bromide ...	$N/800$	*H*.	13 ,,	2 mins.
13. Strontium chloride	$N/800$	*H*.	21 ,,	4½ ,,
14. Magnesium sulphate	$N/600$	*H*.	7 ,,	2 ,,

Observations 1 and 2, 1 and 3, and 5 and 6 show clearly that the effect of temperature depends on the quality of the sol. The concentration of the electrolyte has also an effect even for the same sol.

It would appear from table I that the extent to which the time varies with change in temperature differs with different preparations of the sol. For any particular sol, however, the effect of temperature is approximately the same for the different ions within the groups referred to above.

Experiments were made with freshly prepared sols with excess of arsenious oxide, and the results were similar. In all, fifteen different samples have been used, and the results were always concordant. The experiments with excess of arsenious acid show that the effect of temperature cannot be wholly referred to hydrogen sulphide evolved by the decomposition of arsenious sulphide. It is true that rise of temperature increases the rate of decomposition of arsenious sulphide, but the quantity produced in this way is extremely small. Moreover, the rate of evaporation of dissolved hydrogen sulphide also increases. It would appear from what follows that the effect of temperature is rather complex, and a slight change in the quantity of hydrogen sulphide cannot explain it. It may be pointed out that freshly prepared sols have no perceptible odour of hydrogen sulphide at any of the temperatures investigated, and that the magnitude of the effect observed would require a rather marked change in the concentration of dissolved hydrogen sulphide.

With aluminium sulphate and thorium nitrate, more complicated results were obtained. In some cases, an increase of temperature increases the time, and in other cases the reverse is the case. With a particular sample of the sol and a particular concentration of electrolyte, different readings agreed with one another perfectly. On closer investigation, it was found that concentration of the electrolyte, as well as the quality of the sol, have to be taken into consideration. It must also be remembered that a dilute solution of aluminium sulphate "ages" considerably with time, as pointed out by Powis (*Zeitsch. physikal. Chem.*, 1914, **89**, 106). The combined effect of "ageing" of the sol and the electrolyte will be apparent from table II, in which the time for coagulation diminishes with $1{\cdot}064N/9000$-aluminium sulphate from six and a-half minutes to two and a-half minutes eleven days later, but the influence of temperature is the same in both cases.

TABLE II.

Electrolyte, Aluminium Sulphate.

		Corresponding times at different temperatures.		
Concentration.	Sol.	Room temperature.	25°.	45°.
$1{\cdot}064N/7000$	*I*	3 mins.	2 mins.	1½ mins.
$1{\cdot}064N/9000$	*I*	6½ ,,	—	More than 12 mins.
$1{\cdot}064N/9000$	(11 days later)	2½ ,,	—	4 mins.
$1{\cdot}064N/10000$	*I*	6 ,,	—	17 ,,
$1{\cdot}064N/10000$	*D*	15 ,,	—	3 hrs. 28 mins.
$N/5000$	*J*	> 2 hrs. 41 mins.	57 mins.	1 hr. 26 mins.

Table III records some similar data with thorium nitrate. Similar irregularities will be noticed here. It would seem that a change in temperature produces independent changes in several factors which govern the mechanism of coagulation.

TABLE III.

Electrolyte, Thorium Nitrate.

Concentration, in grams of the crystallised salt per litre.	Sol.	Corresponding times at different temperatures. 4°.	28°.	8°.
0·025	A	4 mins.	1 min. 30 secs.	More than 2 hrs.
0·02	A_1	11 ,,	28 mins.	Not in 12 hrs.
0·0175	A_1	31 ,,	Not in 2 hrs.	—

Sols A and A_1 are of the same sulphide content, but prepared on different dates.

Experiments with Sols containing Ethyl Alcohol and Phenol.

Kruyt and Duin (*Koll. Chem. Beihefte*, 1914, 5, 269) investigated the effects of adding substances like ethyl alcohol, *iso*amyl alcohol, and phenol, which diminish the surface tension (air–liquid surface) of water. They used them in concentrations varying from $N/50$ to $3N/10$. It is needless to point out that in such concentrations most of the physical properties of the dispersion medium will be altered. Their work has an interesting bearing on the results recorded here in so far as they also found that the bivalent group of cations act in a different manner from the uni- and ter-valent groups. In fact, they observed the reverse effect, namely, an increase in stabilisation with the barium group and a decrease with the rest.

Experiments at three different temperatures with potassium chloride, barium chloride, strontium chloride, calcium bromide, magnesium sulphate, aluminium sulphate, and thorium nitrate were made with sols containing small quantities of alcohol and phenol.

To a definite volume of a sulphide sol was added a definite volume of a solution of alcohol or of phenol of known strength, and in a blank experiment water was added in the same ratio.

With potassium and the bivalent cations exactly the same results were obtained as with the ordinary sols, that is, an increase in stability with rise of temperature for potassium and a decrease in the case of the bivalent cations. The concentration of phenol in the sol was about 0·515 gram in 100 c.c., and that of alcohol varied

from 5 c.c. to 25 c.c. of absolute alcohol in 100 c.c. of the sol. With the small quantities of phenol used, no noticeable change was observed from the blank experiment, but with alcohol a slight decrease in stability for potassium and a slight increase with the bivalent cations were noticed. This is in agreement with the observations of Kruyt and Duin (*loc. cit.*), but the magnitude of the change is small.

With alnminium sulphate and thorium nitrate, more complicated results are obtained, as is to be expected from the temperature-effect with the pure sols, and they will be dealt with on a future occasion.

A few selected data are given in table IV.

TABLE IV.

Electrolyte, Strontium Chloride. Concentration, N/800.

	Corresponding times.		
	0–2°.	28°.	65°.
Sol (with water)	1 hr. 15 mins.	21 mins.	4½ mins.
Alcohol present	,,	30 ,,	4½ ,,
Phenol ,, ...	,,	20 ,,	3½ ,,

Calcium Bromide, N/800 *approximately.*

Sol with water	1 hr. 18 mins.	10 mins.	2 mins.
Alcohol present	1 hr. 23 mins.	22 ,,	2 ,,
Phenol ,, ...	1 hr. 15 ,,	13 ,,	About 2 mins.

Magnesium Sulphate, N/600.

Sol with water	35 mins.	7 mins.	2 mins.
Alcohol present	34 ,,	7 ,,	1½ ,,
Phenol ,, ...	33 ,,	6 ,,	About 2 mins.

The hydrosol contained 4·8 millimoles of sulphide per litre.

Discussion of Results.

The different effects observed for different ions may be referred to the selective nature of the adsorption process to which a diminution in the charge of the particles of the colloid is due. The different results obtained with different concentrations of the same electrolyte and with different qualities of the sol show the complicated nature of the phenomena. As the theory of the process of coagulation stands at present, the results may broadly be attributed to three factors:

(1) The increase in the number of collisions with increase in thermal energy and decrease in viscosity.

(2) The increase in the repulsive forces between the particles due to a decrease in the dielectric constant of the medium.

(3) Variations in the adsorbability of the different ions present in solution which may change (*a*) the charge of the particles, and (*b*) the adsorbability of the coagulating ions, which necessarily means a change in the coagulating power.

To these must be added any change in the number of the particles and in the total snrface of the colloid that may take place with change in temperature. Of these various factors, to which the complex nature of the results may be attributed, (1) has been given a mathematical form by Smoluchowski (*Zeitsch. physikal. Chem.*, 1917, **92**, 129); (2) affects all cases equally, and may be accounted for definitely. Regarding variation of adsorption with temperature, Freundlich (*Zeitsch. physikal. Chem.*, 1906, **57**, 385) gives experimental reasons showing the effect to be slight. This seems to be further supported by the experiments of Burton ("Physical Properties of Colloidal Solutions," 1916, 137), who finds that the mobility of colloidal particles of silver is inversely proportional to the viscosity at different temperatures. This would mean that the charge is constant. The experimental error in his experiments is quite large, and small variations are not ruled out. Since all the other factors affect the different cases equally, it must be concluded that there is a variation in the adsorbability of the coagulating ions to account for the different effects observed with different ions. As there are several opposing factors operating, it is not possible to say whether a decrease or an increase in adsorbability has occurred. If the net result of the other factors is an increase in the stability of the sol, that is to say, a smaller number of successful collisions, then we have to assume that, in the case of potassium or aluminium ions, either (*a*) the adsorbability has decreased, or (*b*) if it has increased, the increase is quite insufficient to counterbalance the stabilising effect due to other causes.

Similar considerations show that nothing can be said as to the direction of change in adsorbability if the net result is in the opposite directions.

In the case of the ions of the barium group and the hydrogen ion, it is evident that the change in adsorbability is relatively more in favour of instabilisation.

However, our ideas regarding the mechanism of this adsorption are vague and indefinite. Even the fundamental assumption that the equality in charge corresponds with a definite rate of coagulation for the different ions is not on very secure ground. There is, of course, much experimental evidence in its favour, but direct experiments on the migration velocity are few. Indeed, Powis

(T., 1916, **109**, 734) obtained a markedly different value of the contact potential for potassium chloride (0·044 volt) from those with other salts (0·026—0·024 volt), corresponding with the same rate of coagulation. What is needed is a more detailed examination of the process of coagulation in all its aspects, and a mathematical formulation of the assumptions made in the simplest form of the theory as developed by Hardy, Freundlich, Bredig, and Smoluchowski.

Summary.

(1) A rise in temperature has different effects on the rate of coagulation, depending on the nature of the electrolyte, the quality of the sol, and the concentration of the electrolyte. These effects are not due to any irreversible change in the sol.

(2) The salts of the alkali metals show a stabilisation at higher temperatures; the salts of the alkaline earth metals always show a diminution in stability, the same being also the case with sulphuric and hydrochloric acids. The same results are obtained even when the sol contains small quantities of alcohol or phenol in solution.

(3) With aluminium sulphate and thorium nitrate, the quality of the sol and the electrolytic concentrations determine the effect of temperature, and both an increase or a decrease in stability is met with, as the case may be. In the presence of traces of alcohol or phenol, the results are more complicated.

(4) Effects of temperature are small compared with the effect of valency, and show that a change in the adsorbability of the different ions must be assumed.

My sincere thanks are due to Prof. F. G. Donnan, F.R.S., for his kind interest in the work and for the facilities for carrying it out. I have also much pleasure in thanking my friend, Dr. J. C. Ghosh.

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XLIV.—*The Preparation of Halogenohydrins.*

By John Read and Margaret Mary Williams.

In a previous communication (T., 1917, **111**, 240), we have shown that when ethylene is passed into cold bromine water, two additive reactions occur simultaneously, leading to the production of ethylenebromohydrin and ethylene dibromide respectively. As the first of these reactions takes place with a greater velocity than the second, the method is well adapted to the preparation of ethylenebromohydrin in quantity. Thus, from 200 grams of bromine reacting in a particular experiment, we were able to isolate 85 grams of ethylenebromohydrin and 88 grams of ethylene dibromide, the corresponding relative percentages of ethylene being, therefore, 59 and 41. The bulk of the ethylene thus reacts to form ethylenebromohydrin rather than to produce ethylene dibromide. Owing to the difficulty of effecting a complete isolation of the bromohydrin, the experiments in question are to be regarded as qualitative rather than quantitative, and the latter aspect is reserved for further treatment.

In a further study of the reaction we have now found it possible to improve the yield of bromohydrin by adopting a modification of the original method, to which, incidentally, we have already directed attention (*loc. cit.*, p. 243), that is, by increasing the concentration of the ethylene, and thus accelerating its gross rate of reaction. At the same time, the modified method reduces the concentration of free bromine in the liquid to a minimum throughout the operation.

A current of air is charged with bromine vapour by causing it to pass slowly through a vessel containing an appropriate quantity of the halogen. The gaseous mixture is then passed through a perforated glass bulb into ice-cooled water, which is subjected to vigorous mechanical stirring throughout the course of the experiment. A second perforated bulb, arranged at a distance from the first, admits a regular stream of ethylene into the liquid in the form of numerous minute bubbles. Reaction occurs readily under these conditions, the bromine being admitted at a rate sufficient to maintain at the most a barely perceptible tint in the liquid. The operation may be conducted for a considerable time, and naturally, in practice, the most effective period will be determined by the influence exerted on the reaction by the steadily increasing concentration of ethylenebromohydrin and hydrogen bromide in the solution. This aspect of the reaction is still under consider-

ation, but it may here be noted that in both the original and the *modified method* the process was continued until the solution had attained a concentration of somewhat more than 14 per cent. of ethylenebromohydrin, determined by direct isolation, the mean value corresponding approximately with a 1·33*N*-solution of this substance.

The following results of a typical experiment may be quoted, the products having been separated in the manner already described (*loc. cit.*, p. 242): using 500 c.c. of water, the amounts of ethylenebromohydrin and ethylene dibromide obtained were 82 grams and 54 grams respectively, and the amount of hydrogen bromide present in the liquid at the end was 69·7 grams, estimated by titration. The relative percentage amounts of ethylene corresponding with the above weights of ethylenebromohydrin and ethylene dibromide are 70 and 30 respectively. It is apparent, therefore, that the modified process is superior to the original method in yielding an appreciably higher bromohydrin/dibromide value, the molecular ratio being 1·45 in the original method and 2·3 in the modified process.

As already indicated, the results derived in this manner, although useful for purposes of comparison, are not to be accepted as exact *quantitative* values, and possibly a more accurate idea of the numerical relationships may be derived from a consideration of the distribution of the bromine in the above experiment. Of the total bromine acconnted for (167·3 grams), 62·7 per cent. was utilised in the production of the isolated bromohydrin and 27·5 per cent. was converted to dibromide, whilst the residual 9·8 per cent. represents an apparent excess of hydrogen bromide, the occurrence of which may possibly be due in some measure to decomposition of hypobromous acid into hydrogen bromide and oxygen. Under the conditions now described, however, it seems unlikely that any very appreciable loss of halogen would accrue from this cause; the apparent excess of hydrogen bromide appears rather to be a consequence of the incomplete extraction of the soluble bromohydrin. Accepting this view, that is, adopting the amount of hydrogen bromide formed as a criterion of the yield of bromohydrin, the distribution of the ethylene in the experiment described above would be 75:25, corresponding with a molecular ratio of 3·0 as between ethylenebromohydrin and ethylene dibromide.

Further discussion of these values may conveniently be deferred until further data have been accumulated, but the results prove that cold bromine water provides a valuable source of potential hypobromous acid, and that its application in the manner described opens up a very practical and expeditious method of preparing

bromohydrins. That this additive reaction is capable of wide application is indicated by the results of further investigations, which, however, for the most part have not yet been completed. In the case of cinnamic acid, for example, we have been able to show that a similar reaction occurs with great ease, the ratio of the respective amounts of cinnamic acid converted to bromohydrin and dibromide in a particular experiment being about 5·0 (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 561). Owing to the comparatively high molecular weights of the substances concerned, and also to the ease with which the products may be isolated, the final concentration of bromohydrin in the solution was kept in this case quite conveniently below 0·2*N*; the high value of the bromohydrin-dibromide ratio is doubtlessly due partly to this factor.

From the results we have recorded in the case of bromine water, it is evident that chlorine water may similarly be regarded as a highly convenient source of potential hypochlorous acid for use in the preparation of the corresponding chlorohydrins. Bromine rather than chlorine was selected for the initial investigation, owing to the reported comparative facility of combination of hypobromous acid with ethylene (*Annalen*, 1866, **144**, 40; *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900), and to the greater convenience of manipulation. Our anticipation that chlorine water and ethylene would react similarly was confirmed by a series of preliminary experiments, but, owing to the pressure of other work, the matter had to be left in abeyance for the time being. The continuation of this line of our investigation has now been rendered unnecessary, owing to the recent publication by Gomberg (*J. Amer. Chem. Soc.*, 1919, **41**, 1414) of the results of a detailed examination of this reaction, the principle adopted being that laid down in our original paper, whilst the amounts of ethylenechlorohydrin produced were estimated by means of a refractometric method which appears to meet adequately the requirements of this particular case. From the results given, it would seem that under comparable conditions the reaction in the case of ethylene proceeds somewhat more readily with chlorine water than with bromine water, interpolation revealing that in the preparation of a 1·33*N*-solution of ethylenechlorohydrin, the relative percentage amounts of ethylene converted to chlorohydrin and dichloride would be 84 and 11 respectively.

It may be added that a study of the action of chlorine water on cinnamic acid has also given satisfactory results. The details of this last reaction, as well as the results of an extended series of related investigations, are reserved for future publication, but we may remark in this place that sufficient data have been secured to

indicate that both chlorine water and bromine water are capable of wide application in the novel and effective method of preparing halogenohydrins which we have described.

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XLV.—*The Activation of Wood-charcoal by Heat Treatment.*

By JAMES C. PHILIP, SYDNEY DUNNILL, and OLIVE WORKMAN.

THE observation that the absorptive power of wood-charcoal is notably increased by prolonged heating was made by one of the authors in the course of investigations aiming at the improvement of defence against poison gas (see Philip, *J. Roy. Soc. Arts*, 1919. **67**, 126; Winter and Baker, this vol., p. 319). This fact of activation by heat treatment has, however, considerable significance also from the technical point of view, and, further, raises many interesting questions of a purely scientific kind. The present paper contains a brief preliminary record of work carried out with the object of elucidating the extent and the mechanism of the activation effected by heat treatment alone, and divides itself naturally into two parts, which deal respectively with experiments on the absorptive power of wood-charcoal for (*A*) sulphur dioxide, (*B*) methylene-blue in aqueous solution.

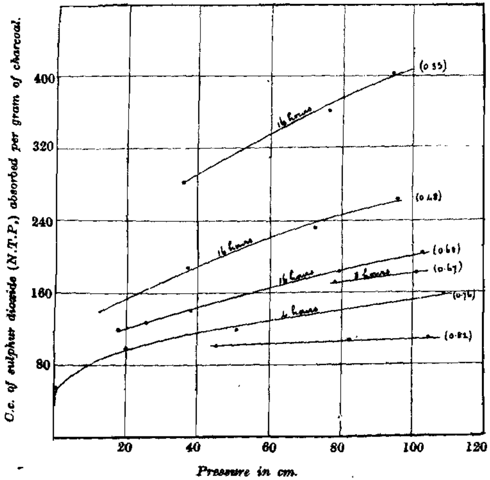
A.

The main series of experiments was carried out with birch-charcoal, and the stock material was prepared by heating small cubes of the wood for three hours at 800°. The product was broken up and screened, the granules which passed through a 0·25 cm. mesh (0·1 inch), but were kept back by 0·125 cm. mesh (0·05 inch), being used in the tests.

For a determination of absorptive power under different pressures, a portion of these granules was placed in a Jena-glass tube which, by means of a T-piece and appropriate stopcocks, could be connected either with a vacuum pump or with a gas-burette containing sulphur dioxide and provided with a long pressure gauge. The tube with the charcoal was first exhausted at a dull red heat for a short time, and then, on cooling, the charcoal was weighed in a vacuum. On putting the glass tube with the char-

oal again in position and immersing it in melting ice, the dead pace (of known volume) between the stopcocks and the glass tube ras thoroughly exhausted and the connexion with the pump was losed. The sulphur dioxide in the gas-burette was then admitted o the dead space and the charcoal, and equilibrium was allowed to stablish itself at a number of different pressures, the volume of mabsorbed gas for each pressure being read off on the gas-burette,

FIG. 1.



with an allowance for the volume of the dead space and the glass tube.

The isothermal volume–pressure relationship thus obtained for the original stock charcoal appears in Fig. 1 as the lowest curve (marked 0·82). The other curves in this figure are the corresponding isotherms (all at 0°) obtained, in the same way as already described, for portions of the stock material which had been heated for the different periods indicated. It is clear that, in general, the absorptive power of the charcoal for sulphur dioxide is increased

by this treatment, but it is equally plain that the duration of the heating is not the main factor in determining the degree of activation.

The clue to this factor is to be found in the alteration of the bulk density which results from the heating of the charcoal (compare Lamb and others, *J. Ind. Eng. Chem.*, 1919, **11**, 427; *Chem. News*, 1919, **119**, 283). Experimental evidence for this is furnished by the figures of the bulk density of all charcoals for which volume–pressure relationships are recorded in Fig. 1. A glance at the values for the *relative* bulk density (added in brackets at the ends of the corresponding curves) shows that the order of activity for birch-charcoals is very nearly the order of the bulk density, and is not determined primarily by the duration of the heating. The conditions under which the charcoal is heated can be widely modified, air being excluded in varying degrees according to the method of packing and covering, and it was proved conclusively that the greater the facilities for the access of air to the heated material, the greater is the decrease of bulk density and the greater the increase in absorptive power. Thus, for example, if a quantity of the original stock charcoal in the form of granules was heated in a crucible for a long period, the portion occupying the bottom of the crucible being separated from the rest by a layer of asbestos, and being thus better protected against circulation of air, it was found that the product from the upper part of the crucible had a lower bulk density and was considerably more active than that from the bottom.

The view that the degree of activation is intimately connected with the extent to which the charcoal is oxidised during the heating is strengthened by experiments made with charcoal from which air was excluded during the exposure to a high temperature. For this purpose, a Jena-glass tube containing a sample of charcoal was freed from air by a current of nitrogen, introduced into an electrically heated furnace, and sealed up about half an hour later. The heating continued for twenty hours, and it was then found that both the absorptive power and the bulk density were practically unaltered. A slight oxidation, even under these conditions, is probably unavoidable, for, as Rhead and Wheeler's work has shown (T., 1913, **103**, 461), it is impossible to heat carbon without getting at least some quantity of the oxides.

Another interesting feature of the curves in Fig. 1 is the change in their character with increasing degree of activation. Whereas with the original, comparatively inactive stock charcoal an increase of pressure above a certain value does not lead to any marked increase of gas absorption, with the most active charcoals there

appears to be no such limit: the slope of the volume-pressure curve becomes steeper as the activation increases.

The observations recorded above appear to be capable of a comparatively simple explanation—an explanation adopted as a working hypothesis by one of the authors (S. D.) during the experimental exploration of the question. According to this view, which differs somewhat from that of the American workers already quoted, the heating of charcoal results in the widening, by progressive oxidation, of the capillary channels with which the granules are riddled. In this way, although the external volume of a granule is practically unaltered, its bulk density is diminished, and the effective surface is enormously increased. For a charcoal of low activity, which, on this view, has extremely narrow capillaries, the deposition of a comparatively shallow layer of gas molecules on the surface will block the capillaries and cut them off from further participation in the absorption process. Increase of pressure in such a case will have very little effect in increasing the absorption, because of the very restricted surface left available. In an activated charcoal, on the other hand, the capillaries have been opened up, and the deposition of additional gas molecules accompanying an increase of pressure can proceed along the walls of these internal capillaries as well as on the free surface of the charcoal. The limit, therefore, of the absorption must lie at a higher pressure than for a charcoal of low activity, and this is what is found experimentally.

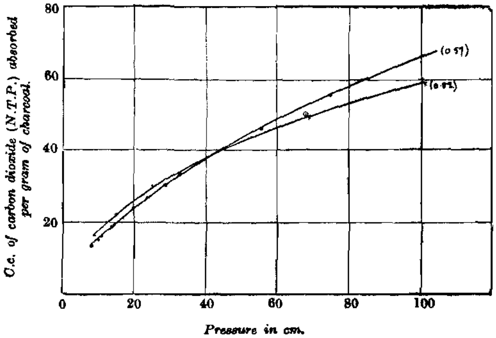
If the foregoing interpretation has any basis in fact, then for low pressures far from the saturation limit, where the molecules of absorbed gas form, presumably, only a shallow layer on the surface of the charcoal, there should be but little difference between activated and unactivated material, even where a notable difference in favour of the activated material develops at higher pressures. This conclusion was confirmed by some experiments on the absorption of carbon dioxide by charcoal at 25°, and the results obtained with two samples of relative bulk densities 0·82 and 0·57, respectively, are shown in Fig. 2. It appears that the charcoal of lower bulk density, although more active at higher pressures, is at lower pressures actually somewhat less absorbent than the unactivated material.

B.

The increase in the absorptive power of wood charcoal for gases effected by continued heating is paralleled by a marked increase in the power of the charcoal to remove methylene-blue from its aqueous solution.

For the purpose of comparing the efficiency of different specimens of charcoal from this point of view, a uniform procedure was adopted. Each sample to be examined was ground in a mechanically-driven agate mortar, and 0·5 gram of the product was then agitated for three hours on a mechanical shaker with a given quantity of a standard methylene-blue solution. Thereafter the solution was filtered, and the residual methylene-blue was determined by titration with titanium chloride. The period of three hours was chosen for the shaking because it was found that, although slight subsequent adsorption of the dye occurred, by far the greater part of the process had been completed in the period

FIG. 2.



mentioned. Moreover, the object was to get a measure of the *comparative* activity of the charcoals, and it was therefore not considered necessary to carry the adsorption to its limit.

The magnitude of the activation effect is shown by the figures given below, which were obtained with Japanese ash charcoal. The wood was first carbonised at 925° for one hour, and a sample of the product (0·5 gram, as in all other cases) was tested for its decolorising power, as described above. The bulk of the product was further heated for eleven hours at 925°, and a sample was again examined. The material was heated subsequently for periods of sixteen, six, eight, and seven hours, in each case at 830°, a sample

being taken and examined at each stage. The results are embodied in the following table:

Total time of heating in hours	1	12	28	34	42	49
Percentage of dye removed from solution	0·6	14·7	24·4	42·5	51·8	60·3

A sample of commercial animal-charcoal, tested under precisely the same conditions, removed 17·8 per cent. of methylene-blue, and it appears, therefore, that the exceptional activity commonly attributed to animal-charcoal can be paralleled, and even surpassed, by a heat-treated wood-charcoal.

Attempts have been made (Glassner and Suida, *Annalen*, 1907, **357**, 95; Knecht and Hibbert, *J. Soc. Dyers and Col.*, 1916, **32**, 226) to correlate the activity of a charcoal in decolorising solutions with its nitrogen content, but the probability of any such relationship must be regarded as exceedingly small in view of the above figures for a wood-charcoal. Further, the charcoal prepared from pure sucrose can be activated in the same way, as was shown by experiments with the original sugar-charcoal employed by Winter and Baker (*loc. cit.*) in their study of the absorption of sulphur dioxide. A sample of this charcoal, tested exactly as has been described, removed only 1 per cent. of methylene-blue from the standard solution. A portion which had been heated at 870° for two hours removed 3·8 per cent., and a portion similarly heated for twenty hours removed no less than 45·4 per cent. of the dye.

The decolorising power of a charcoal appears to be primarily determined by its physical structure and its surface development, and not by the presence of any specific admixture. The efficiency of animal-charcoal itself is a function of the heat treatment it has received, and can be increased to a very notable extent. Thus, the sample of animal-charcoal which, as already stated, removed 17·8 per cent. of methylene-blue from solution, removed 69·6 per cent. after being heated for eighteen hours at about 800°. Special charcoal preparations, such as eponite, exhibit similarly a big increase of decolorising power as a result of heat treatment.

The absorptive power of a charcoal has sometimes been associated with the presence of specific inorganic constituents in the ash, but the results of certain experiments made with Japanese ash charcoal show that this is a factor of very minor significance. The experiments consisted in a comparison of purified and unpurified material, both before and after heating. The unpurified charcoal (*A* in the following table), containing 4·45 per cent. ash, was digested with hydrochloric acid, then thoroughly washed, and dried. This treatment gave a product, *B*, the ash content of which was 1·19 per

cent. The activities of A and B, as well as of the products A_1 and B_1, obtained by heating A and B, respectively, for four hours at about 1000°, are recorded in the table.

Charcoal.	Relative bulk density.	Percentage of methylene-blue removed from solution.
A	—	12·9
A_1	—	31·5
B	0·56	13·2
B_1	0·47	33·2

It is clear that the quantity of the ash makes very little difference either to the original absorptive power or to the degree of activation effected by heating. In harmony, further, with the observations recorded in an earlier part of this paper, the increase of activity is associated with a diminution in the bulk density.

As to the temperature at which the wood or charcoal should be heated to bring about activation, it appears that it must be 800° or above for any rapid improvement to take place. Evidence for this is embodied in the following two tables, in which, it should be noted, each line of figures refers to a portion of the wood (in the form of small cubes) heated independently at the temperature and for the period stated.

Poplar wood at different temperatures.

Temperature.	Duration of heating.	Percentage of dye removed.
370°	2 hours.	0·6
370	5 ,,	0·9
370	17 ,,	1·0
850	2 ,,	5·1
850	5 ,,	11·0

Poplar and willow heated for 2 hours.

Wood.	Temp.	Percentage of dye removed.
Poplar	370°	0·6
,, ...	850	5·1
,, ...	1,000	7·5
Willow	300	1·6
,, ...	600	1·8
,, ...	850	5·0

The variation in the rapidity of activation with the texture of the original wood was investigated, and it was found that whilst the light woods were activated more rapidly, they were ultimately surpassed in activity by charcoals derived from denser woods, such as box. So far as the more rapid activation of the lighter woods is concerned, the following figures are of interest. The temperature of carbonisation was 850° in each case.

Wood.	Time of carbonisation.	Percentage of methylene-blue removed from solution.
Willow	2 hours.	5·0
,, ...	5 ,,	18·3
Poplar	2 ,,	5·1
,, ...	5 ,,	11·0
Box	2 ,,	1·2
,, ...	5 ,,	2·4

Experiments were instituted with the object of finding whether heat alone, apart from oxidation, would lead to any change in the decolorising power of charcoal, and with this in view, various specimens were heated for a prolonged period in a current of nitrogen. It turned out, however, to be impossible to heat these powdered charcoals without their losing considerably in weight and without considerable quantities of carbon dioxide and carbon monoxide being evolved. The products obtained in this way by heating small quantities of the charcoal at 800° for twenty-four hours were found to have diminished in bulk density and to have gained notably in decolorising power, as is shown by the figures below:

Charcoal.	Loss of weight, per cent.	Relative bulk density. before.	after.	Percentage of methylene-blue removed from solution. before.	after.
Japanese ash	34	0·52	0·41	13·0	38·7
Birch	27	0·62	0·48	2·5	16·0
Animal	46	0·41	0·29	17·4	36·4

In view of the pertinacity with which oxygen is retained by charcoal (see Rhead and Wheeler, T., 1913, **103**, 461), it is perhaps not surprising that appreciable quantities of the oxides should be obtained on heating carbon under the conditions stated, but certainly the loss of weight and the increase of activity observed were much greater than was expected from the corresponding experiments recorded in the first part of this paper. It should, of course, be noted that the charcoal was heated as granules in the one case and as powder in the other, and it is possible that this explains the different activation effects observed. This and numerous other points connected with the activation of charcoal by heat treatment still require investigation and elucidation, and further experiments are in progress with this object.

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XLVI.—*The Composition of Salvarsan.*

By Robert George Fargher and Frank Lee Pyman.

Commercial salvarsan is prepared by the reduction of 3-nitro-4-hydroxyphenylarsinic acid by means of sodium hyposulphite, solution of the base in methyl alcohol containing hydrogen chloride and precipitation of the salt by means of ether (Ehrlich and Bertheim, *Ber.*, 1912, **45**, 756).

It is a yellow, amorphous compound slightly variable in chemical composition and more so in physical properties; chemically, it is generally regarded as 3:3′-diamino-4:4′-dihydroxyarsenobenzene dihydrochloride containing combined solvent, but published statements on the details of its composition contain many discrepancies.

When salvarsan was first introduced into general use, the makers, Farbwerke vorm. Meister, Lucius & Brüning, stated that it contained about 34 per cent. of arsenic. In 1911, however, Gaebel (*Apoth. Zeit.*, 1911, **26**, 215) found that it lost 7·6 per cent. of its weight on heating, and contained only 31·2 or 31·8 per cent. of arsenic. He communicated these results to Ehrlich, with the result that the later circulars of the issuing firm bore the corrected statement: "the arsenic content of the preparation corresponds to the formula $C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$."

The Solvent Content of Salvarsan.

Ehrlich and Bertheim (*loc. cit.*) have given the results of analysis of a specimen of salvarsan prepared, not by the technical method, but by reducing 3-amino-4-hydroxyphenylarsenious oxide with sodium amalgam and acetic acid, as follows:

Found: C=32·63; H=4·06; N=6·06; As=31·99; Cl=15·41.
$C_{12}H_{12}O_2N_2As_2,2HCl,MeOH$ requires C=33·1; H=3·8; N=6·0; As=31·85; Cl=15·07.
$C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$ requires C=30·3; H=3·8; N=6·0; As=31·6; Cl=14·9 per cent.

On determining methyl alcohol in 2 grams of this sample, they obtained a "distinctly positive" reaction, and this fact, in conjunction with the percentage of carbon in the compound, led them to put forward the first of the above formulæ for 3:3′-diamino-4:4′-dihydroxyarsenobenzene dihydrochloride prepared in this way.

Recently, Kober (*J. Amer. Chem. Soc.*, 1919, **41**, 442) has claimed that there is no justification for Gaebel's assumption of $2H_2O$ in salvarsan, and is clearly of opinion that the combined

solvent in salvarsan, precipitated from methyl alcohol by means of ether, is methyl alcohol.

Our experiments show that this view is erroneous. On analysis of two samples of salvarsan precipitated from methyl-alcoholic solution by means of ether, we obtained the following figures:

(*A*) C = 29·5; H = 4·0; Cl = 12·3; S = 2·89; As = 30·9; ash = 0·43; loss in a vacuum = 7·6.

(*B*) C = 29·2; H = 4·1; Cl = 12·0; S = 2·76; As = 31·0; ash = 0·79; loss in a vacuum = 7·7 per cent.

Determination of the ratio C to As gives the results 5·97 to 1 and 5·89 to 1 respectively, which show that the total carbon content of the product is accounted for by the six carbon atoms of the benzene nucleus attached to each atom of arsenic.

These results contradict Kober's assumption that the combined solvent in salvarsan consists of methyl alcohol, and are confirmed by direct determinations of the methyl alcohol by the method described by Simmonds (*Analyst*, 1912, **37**, 16), and later modified by Jones (*ibid.*, 1915, **40**, 218), when percentages of methyl alcohol varying from nil to 1·4 per cent. were found.*

It may be noted here that when salvarsan is precipitated from methyl-alcoholic solution by means of acetone, the product contains one molecular proportion of acetone, which cannot be removed in a vacuum at the ordinary temperature, and, beyond this, the usual amount of water which can be removed in a vacuum. The acetone was estimated by distilling the compound with water and determining the volume of $N/10$-iodine required to convert the acetone in the distillate into iodoform.†

Mean values found: In air-dried substance, acetone = 10·9; loss in a vacuum = 6·1; in dried substance, acetone = 11·2.

$C_{12}H_{12}O_2N_2As_2,2HCl,C_3H_6O,2H_2O$ requires C_3H_6O = 10·9; $2H_2O$ = 6·8.

$C_{12}H_{12}O_2N_2As_2,2HCl,C_3H_6O$ requires C_3H_6O = 11·7 per cent.

* The method consisted in distilling from an aqueous solution of salvarsan (1 in 20 to 1 in 40), half its volume of liquid and determining methyl alcohol in the distillate. Experiments on the delicacy of the reaction confirmed the figures given by Jones (*loc. cit.*), and indicated that in our experiments as little as 0·2 per cent. of methyl alcohol, expressed in terms of the salvarsan employed, should have been readily detected.

† This method of estimation is the subject of a recent communication by L. F. Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39), who includes a summary of previous literature. The results confirm our experiments on the accuracy and delicacy of the estimation.

The Sulphur Content of Salvarsan.

The presence of a considerable proportion of sulphur in commercial salvarsan—not disclosed in the reputed formula—calls for comment. Ehrlich and Bertheim (*Ber.*, 1911, **44**, 1264; 1912, **45**, 762) mention that crude salvarsan base, prepared by means of hyposulphite, contains inorganic matter and slight quantities of a substance containing arsenic united with sulphur, but indicate that these impurities are removed by converting the base into the hydrochloride. Myers and Du Mez (*U.S.A. Public Health Reports*, 1918, **33**, 1003), and Kober (*loc. cit.*), have recently recorded the bare fact that commercial salvarsan contains sulphur.

Several years ago the present authors (compare Medical Research Committee, *Special Report Series*, No. 44, "Reports of the Special Committee upon the Manufacture, Biological Testing, and Clinical Administration of Salvarsan and its Substitutes," No. 1, p. 8) found that commercial salvarsan of both British and German origin invariably contained sulphur, of which the amount varied from 1 to 2 per cent., and, exceptionally, up to 3 per cent. In our opinion, the sulphur occurs at least in part in the form of the sulphamo-group, $\cdot NH\cdot SO_3H$. Our reasons for this view are as follows:

(1) It is well known that the reduction of nitro-compounds with hyposulphite in alkaline solution leads, sometimes in part and sometimes wholly, to the formation of sulphamic acids of the type $R\cdot NH\cdot SO_3H$. Karrer (*Ber.*, 1915, **48**, 1061) states that "nitrocarboxyphenylarsinic acid does not give the normal arseno-derivative when reduced with hyposulphite, but gives an easily soluble substance, probably a sulphamic acid, as has frequently been observed in other cases." Moreover, in the somewhat analogous case of 3:5-dinitro-4-aminophenylarsinic acid, an alkali-soluble reduction product containing sulphur has been obtained which, on treatment with warm acids, yields free sulphur dioxide and salts of hexa-aminoarsenobenzene (E.P. 8041 of 1913). Although no constitution is assigned in the patent, Giemsa (*Deut. med. Woch.*, 1919, **45**, 95) describes the product as a monosulphamic acid of hexa-aminoarsenobenzene, $HSO_3\cdot NH\cdot C_6H_2(NH_2)_2\cdot As_2\cdot C_6H_2(NH_2)_3$.

(2) Whilst Ehrlich and Bertheim's analysis of pure, as distinct from commercial, salvarsan shows a chlorine content of 15·4 per cent., we have found considerably less chlorine in commercial salvarsan of both British and German origin, the content of samples taken direct from sealed ampoules varying generally from 12·5 to 14·5 per cent. It is thus always lower than that calculated for $C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$, which requires $Cl = 14·9$ per cent.,

d, moreover, is usually lower than that necessitated by the utralisation value (that is, the number of parts of sodium hydride required to neutralise 100 parts of salvarsan to phenolthalein). The difference between the chlorine found on estimion and the quantity corresponding with the acidity of salvarsan ust be due to some other acid. The fact that salvarsan forms a paringly soluble sulphate led us to test for the presence of sulphate the product, but only negative results, or, at most, indications f traces, were obtained. In view of the evidence of the formation f sulphamic acids in analogous cases, we believe that that part f the acidity of salvarsan which is not due to the hydrochloric cid is due to the presence of the sulphamo-group.

Determinations of sulphur, chlorine, and neutralisation value in en consecutive preparations, with the results deduced from them, are given below. They are typical of many others.

S.	Cl.	Neut. val.	Cl calculated from neut. val.	Difference in chlorine.	Whence S as $NH{\cdot}SO_3H$.	Other S.
1·7	14·0	16·45	14·57	0·57	0·51	1·19
1·3	14·1	16·25	14·40	0·30	0·27	1·03
1·26	14·06	16·35	14·50	0·44	0·40	0·86
1·48	13·5	16·36	14·51	1·01	0·91	0·57
1·36	13·8	16·34	14·49	0·69	0·62	0·74
1·44	13·7	16·42	14·54	0·84	0·76	0·68
1·47	13·06	16·45	14·57	1·52	1·37	0·10
1·51	13·66	16·47	14·59	0·93	0·84	0·67
1·77	13·23	16·21	14·35	1·12	1·01	0·76
1·74	13·51	16·35	15·50	0·99	0·89	0·85

The possibility, in the case of salvarsan, of the transformation of the sulphamic acid into a true sulphonic acid would seem to be precluded by the conditions of the experiment, which, from a study of the literature, do not appear to favour the change.

The formation of an internal imide, $R{\cdot}NH{\cdot}SO_2{\cdot}NH{\cdot}R$, receives, at first sight, support from the low neutralisation values sometimes encountered, but these are more probably due to partial hydrolysis of the dihydrochloride. We have found that reprecipitation of the hydrochloride from methyl-alcoholic solution leads to a product containing rather less chlorine, whilst the chlorine content, when low, is raised by reprecipitation in presence of a further quantity of hydrogen chloride.

Thus, 8·9 grams of 3-nitro-4-hydroxyphenylarsinic acid were reduced in the usual manner, and the resulting base was dissolved in 100 c.c. of methyl alcohol containing 1·13 grams of hydrogen chloride. From a part of the solution, salvarsan was precipitated immediately by the addition of ether (fraction *A*). To 25 c.c. of the remainder a further quantity of 0·2 gram of hydrogen chloride

was added, and the liquor kept overnight before precipitation (fraction *B*). Both fractions were dried under the same conditions and analysed. Found, in *A*, Cl = 13·6; in *B*, Cl = 14·9 per cent.

Another instance is supplied by a commercial sample of high sulphur content. It contained Cl = 12·3; S = 3·1 per cent. 1·2 Grams were kept overnight in 10 c.c. of methyl alcohol containing 0·2 gram of hydrogen chloride, aud then precipitated by ether. The product contained 13·5 per cent. of chlorine and 2·8 per cent. of sulphur.

(3) Many attempts, both synthetic and analytic, were made to isolate the compound containing sulphur in acid form. Analysis of the commercial hyposulphite employed in the reduction revealed the presence of sulphate, sulphite, thiosulphate, and sulphide as impurities containing sulphur, these, with the exception of sulphide, having been recognised previously by Binz and Sondag (*Ber.*, 1905, **38**, 3830). Increase of the proportion of each in the reduction mixture was without material effect on the sulphur content of the product, and since it was found that the reduction of 3-amino-4-hydroxyphenylarsinic acid with hyposulphite led to a substance *containing relatively little sulphur* (0·34 *per cent.*), *it was concluded* that the acidic sulphur originates during the reduction of the nitro-group by the hyposulphite, a conclusion in harmony with our view of its mode of combination.

Eventually, however, we found that commercial salvarsan, and indeed all specimens prepared by the reduction of 3-nitro-4-hydroxyphenylarsinic acid with hyposulphite, gradually separated to some extent from concentrated methyl-alcoholic solution, this property being much less marked in the preparation obtained by reduction of the amino-acid by hyposulphite and absent in that prepared by the reduction of the amino-acid by hypophosphorous acid. Preliminary *examination of the precipitates showed that they* contained a greater proportion of sulphur than the parent substance, and were practically insoluble even in excess of methyl alcohol. The isolation of this sparingly soluble portion in a state of comparative pnrity was accomplished with some difficulty. Ten grams of a specimen of commercial salvarsan (containing Cl = 13·7; S = 1·0; As = 33·0 per cent.) were dissolved in 50 c.c. of methyl alcohol and kept overnight in an inert atmosphere. The deposit was separated centrifugally, very thoroughly washed with methyl alcohol, and dried in a vacuum. It amounted to 0·4 gram of a bright yellow powder, somewhat sparingly soluble in water and insoluble in methyl alcohol. On analysis, it gave the following results:

Found: Cl = 6·84; S = 5·1; As = 30·8*; neutralisation value = 15·5.*

The combination of a low chlorine content, a high sulphur content, and a normal neutralisation value prove the presence of acidic sulphur. It may be pointed out, further, that the product approximates in composition to the monohydrochloride of the monosulphamic acid of 3:3′-diamino-4:4′-dihydroxyarsenobenzene, the formation of which would be expected in view of Bertheim's statement (*Chem. Zeit.*, 1914, **38**, 756) that a mixture of two arsinic acids gives on reduction only the unsymmetrical arsenobenzene.

$C_{12}H_{12}O_5N_2SAs_2$,HCl requires Cl = 7·3; S = 6·6; As = 31·1 per cent.; neut. val., 16·6.

The remainder of the sulphur is probably attached to arsenic, this mode of combination being indicated by the fact that the distillate from an acid solution of salvarsan often contains traces of hydrogen sulphide, which can be detected by lead acetate and other reagents, whilst 3-amino-4-hydroxyphenylarsenic trisulphide (D.R.-P. 253157) appears to give up at least part of its sulphur as hydrogen sulphide on boiling with dilute hydrochloric acid.

It should be remembered, however, that salvarsan has been shown to possess some of the properties of a colloid (compare Karrer, *Ber.*, 1919, **52**, [*B*], 2319), and it is therefore possible that a portion of the sulphur unaccounted for by the sulphamo-group may be present in physical association with the compound.

The Preparation of 3:3′-*Diamino*-4:4′-*dihydroxyarsenobenzene Dihydrochloride.*

During the progress of the foregoing experiments, it became necessary to prepare pure, as distinct from commercial, salvarsan.

The reduction of 3-amino-4-hydroxyphenylarsenious oxide to the arsenobenzene by means of sodium amalgam in acetic acid had already been described by Ehrlich and Bertheim (*loc. cit.*), and this and several other modifications involving the reduction of 3-nitro-4-hydroxyphenylarsinic acid step by step were investigated.

The first series of experiments involved the preliminary reduction of the nitro-group without affecting the arsinic acid group, leading to 3-amino-4-hydroxyphenylarsinic acid. This had been accomplished by Ehrlich and Bertheim (*loc. cit.*) by means of sodium amalgam, and we employed this process until it became

* Owing to the small amount of substance available these results are only approximate.

evident that, on repeated use, without elaborate purification, the mercury became contaminated with arsenic and the yield of the amino-acid showed progressive diminution. Several other processes, such as cautious reduction with zinc in acid solution, reduction with ammonium sulphide, and reduction with ferrous hydroxide in alkaline solution, were investigated, and eventually we drew the conclusion that the most satisfactory method was to treat the nitro-acid in cold aqueous alkaline solution with just sufficient hyposulphite to reduce the nitro-group (D.R.-P. 224953; Fargher, T., 1919, **115**, 982). The crude product was contaminated with sulphur, but purification as described by Ehrlich and Bertheim (*loc. cit.*) effected the complete removal of this impurity, an important factor in view of our further experiments.

The *reduction of* 3-*amino*-4-*hydroxyphenylarsinic acid* to the corresponding arsenobenzene was readily accomplished by means of hypophosphorous acid, as follows: Five grams of the acid were dissolved in 25 c.c. of hypophosphorous acid (D 1·15) and 25 c.c. of water, 0·1 gram of potassium iodide being added as a catalyst. The resulting solution was heated to 60° for two hours in an atmosphere of carbon dioxide, cooled, made slightly alkaline with 10 per cent. aqueous sodium carbonate, the precipitated base filtered, washed very completely with water, converted into the hydrochloride by solution in methyl alcohol containing hydrogen chloride, precipitated by dry ether, collected, and dried for several hours in a vacuum. The yield amounted to 3·7 grams. The following figures were obtained on analysis:

Found: As = 31·8, 31·84; Cl = 14·15; loss in a vacuum = 6·38.

In the substance dried at 60° in a vacuum:

Found: C = 33·3, 33·0; H = 3·6, 3·4; N = 6·5.

$C_{12}H_{12}O_2N_2As_2,2HCl$ (439·0) requires C = 32·9; H = 2·8; N = 6·4 per cent.

The base dissolved less readily in methyl alcohol containing hydrochloric acid than did that obtained by the reduction of 3-nitro-4-hydroxyphenylarsinic acid with sodium hyposulphite. The dihydrochloride, grey or very pale yellow in colour, was less readily soluble in water or methyl alcohol than the commercial product. Its solution in three parts of methyl alcohol gave no precipitate on keeping out of contact with air. It decomposed at 187° (corr.).

The *reduction of the amino-acid by sodium hyposulphite* was also undertaken, the product, in most of its properties, resembling commercial salvarsan rather than the pure substance. It differed, however, considerably in the readiness with which it precipitated

m concentrated methyl-alcoholic solution, and contained only 4 per cent. of sulphur. Other figures obtained on analysis licated a normal composition.

The second series of experiments, conducted by the converse ocess, namely, reduction of 3-nitro-4-hydroxyphenylarsinic acid 3 : 3′-dinitro-4 : 4′-dihydroxyarsenobenzene and subsequent reducn of the nitro-groups, was less successful.

The first stage was readily accomplished by means of hypophosorous acid essentially as described in D.R.-P. 269886, although e somewhat elaborate precautions taken in isolating the product ensure freedom from the corresponding diamine were found to superfluous, since the reduction of the nitro-group by the addion of potassium iodide to the reduction mixture (D.R.-P. 271894) ould not be confirmed.

Owing to its insolubility, dinitrodihydroxyarsenobenzene could ot be reduced with sodium amalgam in acetic acid solution, and lthough in alkaline solution reduction took place readily, the roduct was unsatisfactory. The base obtained by reducing linitrodihydroxyarsenobenzene in alkaline solution with sodium yposulphite proved somewhat difficult to filter and wash. The ydrochloride prepared from it differed but little from commercial alvarsan.

In conclusion, we are glad to have the opportunity of recording that this work was carried out in collaboration with the technical experts of Messrs. Burroughs Wellcome & Co., and to thank especially Dr. H. A. D. Jowett and Mr. F. H. Lees, F.I.C., for their valuable help and advice in the course of the work.

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XLVII.—*The Solubility of Potassium Bromide in Bromine Water.*

By ALFRED FRANCIS JOSEPH.

IN a paper communicated to the Society in 1913 (T., **103**, 1554), figures were given for the solubility of potassium bromide in nitrobenzene solutions of bromine. It was there shown that whereas this salt is practically insoluble in pure nitrobenzene, a considerable amount could be dissolved in the presence of bromine, owing to the

formation of the readily soluble tribromide, for the existence of which colorimetric evidence was adduced.

In continuation of these experiments, a study of the corresponding aqueous solutions (saturated with respect to potassium bromide) was commenced. This work was, however, interrupted five years ago, and as it is not likely to be resumed, the results obtained are now published.

Solutions saturated with respect to bromine have been studied by Worley (T., 1905, **87**, 1107) for potassium bromide and by Bell and Buckley (*J. Amer. Chem. Soc.*, 1912, **34**, 14) for sodium bromide. For solutions of moderate concentration, the solubility of bromine was found to be greater in bromide solutions than in pure water by approximately one gram-molecule of bromine for each molecule of bromide, and it was shown that this is in accordance with the formation of a tribromide. In the case of concentrated solutions of sodium bromide, however, the ratio of additional bromine to bromide rose to nearly 2·5 : 1, indicating the formation of a higher polybromide.

In the experiments now recorded, the solubility of potassium bromide in bromine water was determined by shaking bromine, water, and an excess of potassium bromide in 250 c.c. stoppered bottles in a 50-litre thermostat provided with a Noyes shaking arrangement for twenty-four hours, the temperature being maintained at 32·4 ± 0·02°.

Solubility of Potassium Bromide in Water.—Several results for the solubility of potassium bromide in water are given in the literature, but they differed sufficiently to make its redetermination worth while at the exact temperature at which these experiments were to be made.

Kahlbaum's best potassium bromide was used, without further purification beyond drying at 150°. It showed only a trace of chloride (less than 0·05 per cent.) when tested by Caven's method of distillation with nitric acid (*J. Soc. Chem. Ind.*, 1909, **28**, 505). The determination was carried out as usual, and the results, expressed as grams of potassium bromide dissolved by 100 grams of water, were:

(*a*) 72·53	(*b*) 72·67	Mean ... 72·56
(*c*) 72·58	(*d*) 72·47	

The figure given in Seidell's "Dictionary of Solubilities," obtained by interpolation between 30° and 40°, is 71·8. Coppet (*Ann. Chim. Phys.*, 1883, [v], **30**, 416) and Etard (*Compt. rend.*, 1884, **98**, 1432) found that the solubility of potassium bromide was a linear function of the temperature; according to the formula of

e former, the result at 32·4° should be 71·05, and according to .e latter 73·43; the value here recorded is very nearly the mean these.

Solubility of Potassium Bromide in Bromine Water.—In these ɛperiments, a portion of the solution was dropped into a flask ɔntaining concentrated potassium iodide solution, the flask and ontents being weighed before and after the addition of the ,romine–bromide solution. The iodine liberated was determined ›y titration with sodium arsenite solution standardised against pure odine. The remainder of the solution was then transferred to a varm cylinder in the thermostat and its density determined approximately by means of the Westphal balance; the figures are probably correct to ±0·0003.

The results are given in the table below.

Grams of bromine per 1000 grams of water.	Grams of potassium bromide per 1000 grams of water.	Density.	Grams of bromine per litre.	Grams of potassium bromide per litre.
0·0	725·6	1·3917	0·0	585·1
24·0	733·9	1·4063	19·2	587·1
32·1	738·2	1·4070	25·5	586·7
39·6	740·7	1·4132	31·4	588·0
74·3	750·2	1·4356	58·4	589·9
120·9	764·3	1·4633	93·8	593·2
137·2	771·1	1·4753	106·1	596·2
229·7	801·3	1·5236	172·3	601·1
382·1	845·9	1·5980	274·1	606·7

Results.—The numbers in the first two columns are related by the straight line formula: increased solubility of potassium bromide = one-third of the bromine concentration.

If A and B are the total molecular concentrations of bromide and bromine per 1000 grams of water, and S is the solubility of bromide in water alone, the equation is

$$(A-S)/B=0{\cdot}47.$$

The actual values of the fraction found for the eight determinations are:

0·50	0·53	0·44	0·44	Mean ... 0·47
0·53	0·46	0·45	0·42	

The corresponding ratio for nitrobenzene solutions was found to vary from 0·53 to 0·32, indicating a much less close agreement with a linear relationship.

If there were no disturbing factors, the ratio should be calculable as follows, on the assumption that the increase of solubility is due to the formation of potassium tribromide.

In the dissociation equation for the tribromide,

$$k(KBr_3) = (KBr) \times (Br_2),$$

the concentration of the free bromide is constant (S) as the solution is saturated with respect to it; that of the tribromide, obtained by subtracting the former from the total concentration of bromide, is $A - S$, and the free bromine by subtracting this last from the total concentration of bromine, that is, $B - (A - S)$, so that $k(A - S) = S(B - A + S)$, or $(A - S)/B = S/(k + S)$, a constant.

For nitrobenzene solutions, k and S are very small, and neither is known, so that this constant cannot be evaluated. For aqueous solutions, S is 6·1 and k, determined by various methods, about 0·05 (Roloff, *Zeitsch. physikal. Chem.*, 1894, **13**, 327; Worley, *loc. cit.*; Joseph and Jinendradasa, T., 1911, **99**, 274), so that $S/(K + S)$ is a little less than unity.

If this held, nearly one gram-molecule of bromide should pass into solution for every gram-molecule of bromine present. The fact that the actual amount dissolved is only about half a gram-molecule shows clearly enough that a disturbing factor is present, but whether it is reduction of solubility of potassium bromide in water by the common ion of potassium tribromide, or the hydration of bromine, causing a reduction iu the amount of "free" bromine, or some other cause, has not been investigated.

Very Concentrated Solutions.—It was hoped to extend these experiments to the study both of very dilute and of very concentrated solutions. Preliminary work on the latter was carried out as follows.

About 250 grams of potassium bromide, about the same weight of bromine, and enough water for the experiment (the amount in different experiments varied from 5 to 100 c.c.) were left in a stoppered bottle for a few days at the ordinary temperature (28°), after which the heavy, dark liquid was filtered through glass wool and analysed.

The results of two such experiments are given below.

	Percentage by weight.		*Grams per 1,000 grams of water.*		*Grams per litre of solution.*	
	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.
Water	13·5	5·4	1000	1000	347	154
Bromide	28·4	15·1	2104	2796	738	432
Bromine	58·1	79·5	4304	14720	1511	2274
Density	2·596	2·860	—	—	—	—

Potassium bromide appeared to be quite insoluble in pure bromine, and it must therefore be concluded that the water is entirely responsible for keeping these large quantities in solution;

e limit of solvent capacity of the water, even when it constitutes ly 5 per cent. of the solution, has not been reached.

So far as the volume concentration (grams per litre of solution) concerned, the maximum for the bromide has been passed before ie water is reduced to this extent; the concentration of bromine rresponding with this maximum must lie somewhere between 00 and 2000 grams per litre.

Conclusion.—(*a*) The solubility of potassium bromide in water increased by the addition of bromine. For moderate concentraions, about half a gram-molecule of bromide is dissolved for each gram-molecule of bromine added to the water.

(*b*) The limit of the solvent capacity of the water was not reached at bromine-concentrations of more than 2000 grams per litre. There is, however, a maximum volume-concentration of bromide, the corresponding bromine-concentration being somewhere between 200 and 2000 grams per litre.

These experiments were carried out in 1914—1915 at the Ceylon Medical College, and my thanks are due to Mr. W. N. Rae for kindly making the measurements with the hydrostatic balance.

WELLCOME TROPICAL RESEARCH LABORATORIES,
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War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 18TH, 1919.

By JAMES WALKER.

I NEED not say how greatly honoured I feel by the invitation of the Council to deliver one of the lectures connected with the War which are to be given in the present session. The title of my lecture is that suggested by the Council, and the experiences I am about to relate are my own, or rather those of my colleagues, for my part was largely that of an interested spectator. These experiences, however, must have been to a great extent shared by all those engaged on the same problems. I therefore make no claim, on behalf of myself or my colleagues, for any novelty of process or method; indeed, one of the most pleasing features of the explosive manufacture during the war was the pooling of results, whereby each factory derived the benefit of the experiences, not only of other factories, but of the Research Department of the Royal Arsenal, Woolwich, and later also to some extent of the Munitions Inventions Department.

In the early spring of 1915, when the dearth of high explosives was the occasion of public outcry, we in the Chemistry Department of Edinburgh University felt that we might do something to utilise local supplies for the production of trinitrotoluene. The War Office was approached, and the suggestion was favourably received by Lord Moulton, the Director of Explosives Supply, to whom we owe most grateful thanks for constant encouragement and help in our enterprise. A company, named the Lothian Chemical Company, which consisted of Dr. A. C. Cumming, Mr. J. W. Romanes, and myself, was formed to execute a contract for the supply of 150 tons of T.N.T., without the use of fuming sulphuric acid, within a specified time, and work was begun in April, 1915, in a disused chemical factory. The management and staff of the factory were recruited from teachers, graduates, and undergraduates of the University Chemistry Department. The first dispatch of T.N.T. was made in October, 1915, and the contract was completed well within the specified period. Further contracts followed, but as the factory was incapable of any great extension, and was, besides, unsuit-

ably situated in a populous district, we agreed to undertake for the Ministry of Munitions the erection and management of a larger factory in the outskirts of the city, known as H.M. Factory, Craigleith. This factory was originally designed to produce 30 tons of T.N.T. per week, but during construction was expanded to manufacture 50 tons weekly. Production was begun in March, 1917, and by July of the same year 30 tons weekly were being delivered. The manufacture of T.N.T. in the original factory was then discontinued, and the works, after considerable delay, were turned over to the manufacture of calcium nitrate. At the date of the armistice, H.M. Factory, Craigleith, was producing as a maximum 60 tons of T.N.T. weekly.

In this country, sodium nitrate from South America was practically the only source of nitric acid and other nitrates. With the progress of the war, however, the consumption of nitrates continually augmented, and the difficulty of importing nitrate from overseas increased owing to the lessened freightage and submarine risks. It became therefore of the utmost national importance first to economise nitric acid by carrying processes of recovery to the highest possible point of efficiency, and secondly to find home sources of nitrates. It may be said that the first problem was adequately solved, but the solution of the second was only in its initial stage at the conclusion of the war.

Manufacture of Nitric Acid.

1. *From Sodium Nitrate.*

The method we adopted for the manufacture of T.N.T. was a two-stage process, toluene being nitrated first to a degree intermediate between mononitrotoluene and dinitrotoluene, the product being thereafter fully nitrated to trinitrotoluene by the use of concentrated nitric acid and concentrated sulphuric acid. The residual acids from the final process were employed in effecting the first nitration. The nitric acid used was made in the customary way from sodium nitrate and sulphuric acid, and was collected at different strengths, according to the requirements of nitration. Thus at one period seven-tenths of the nitric acid was collected as 94 per cent., and three-tenths as 70 per cent., acid; towards the end of the war nine-tenths was collected as 90 per cent. acid and one-tenth as 60 per cent. acid. The concentration of sulphuric acid employed was generally 92 per cent., 2·6 tons of this acid being used for a charge of 2·75 tons of crude sodium nitrate. The distillation occupied about fifteen hours, but was on occasion carried through in eight. The nitre cake from the stills

contained, on the average, 28 per cent. of potential sulphuric acid and only a trace of nitrate. The loss in manufacture was from 5 to 6 per cent.

[Slides of the plant employed were exhibited, and attention was directed to the valuable work of the Thermal Syndicate in supplying the silica condensing spirals and connexions, which greatly facilitated the manufacture.]

2. *From Ammonia.*

Catalytic oxidation of ammonia by Ostwald's method was the most readily available process for the production of nitric acid and nitrates from home material. Of this process we had a brief and incomplete experience, owing to delay in its adoption on a manufacturing scale.

When ammonia is oxidised by air on the surface of a solid catalyst, such as platinum or ferric oxide, the following main reactions take place:

I. $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.

II. $4NH_3 + 5O_2 = 4NO + 6H_2O$.

[Experiments with a platinum wire catalyst were shown which illustrated the prevalence of one or the other reaction according to the proportion of ammonia and air taken.] The concentration of ammonia in the ammonia–air mixture which gives the most favourable results with platinum lies between 10 and 12 per cent., variations within this limit affecting the yield of nitric oxide but little. On a small scale, a yield of 97 per cent. of the theoretical quantity of nitric oxide was obtained.

The source of ammonia which we employed was 25 per cent. purified ammonia liquor, from which the gas was liberated by steam in an ammonia still of the rectifier type. The ammonia gas was passed through a cooler, then through an iron oxide purifier to remove sulphur compounds, and was finally mixed with air, which was supplied by a blower and measured by passage through a meter. The amount of ammonia in the mixed gases was regulated by the feed of ammonia liquor to the still. Thorough mixing was effected in a chamber provided with baffle plates, and the proportion of ammonia in the mixture was checked by analysis as occasion required. In order to protect the platinum catalyst from dust, and especially from particles of iron rust, which greatly lower its efficiency, the air–ammonia mixture before entering the converter was filtered through a box containing slag wool or glass wool.

The converter containing the catalyst was of the type suggested by the Munitions Inventions Department.* It consisted of a square aluminium box of 30 cm. side, built in sections, and connected by pyramidal adapters to aluminium tubes conveying the gases from beneath and leading them off above. Across this aluminium box was placed horizontally a screen of platinum wire gauze of 32 meshes to the cm., the diameter of the wire being 0·06 mm.

Trials were made with one, two, and three successive gauzes in close proximity to each other, but no definite conclusion as to the best arrangement had been drawn before stoppage of the operations. The catalyst, activated by previous heating, was warmed at one spot by means of a flame. The heat produced by the catalytic oxidation at this spot gradually spread and raised the temperature of the whole gauze until it reached 650° to 700°, when it remained steady. The time taken by the gases to pass through one thickness of gauze was of the order of one-thousandth of a second, and the temperature of the gases passing from the converter was about 400°. The impurities in the by-product ammonia used seemed to have little effect on the catalytic activity of the platinum.

The next operation was to convert the nitric oxide thus produced into nitric acid by means of atmospheric oxygen and water:

$$4NO + 3O_2 + 2H_2O = 4HNO_3.$$

The hot gases issuing from the converter were first passed through wide silica **S**-pipes cooled by a stream of water, and then through pipes of narki metal (iron–silicon alloy) completely immersed in water. The temperature was thereby reduced to about 30°, and the gases passed into the oxidation and absorption towers, which were in principle the same as those used in the recovery of nitrous fumes, to be described in the next section. The first absorption towers were acid towers, and these converted the great proportion of the nitrous gases into nitric acid. The final towers were fed with milk of lime, which yielded the remaining oxidised nitrogen as a mixture of calcium nitrite and nitrate. This mixture was returned and fed, along with water, to the first towers in order that the nitrite it contained might be converted into nitrate by means of the nitric acid formed in these towers, the nitrous fumes evolved passing further along the series and being subject to further oxidation. The nitric acid ultimately collected from the acid towers was converted by neutralisation with milk of lime into

* A description and figure of a smaller type may be found in a report of the Ministry of Munitions entitled "The Oxidation of Ammonia Applied to Vitriol Chamber Plants," London, 1919.

calcium nitrate, which was finally concentrated to the required extent in evaporating pans. At the date of the armistice we had only passed out of the experimental stage and begun large-scale production, 30 tons in all having been made.

Recovery of Nitrous Fumes.

The question of economy of nitric acid in the production of T.N.T. is largely dependent on the recovery of nitrogen contained in the waste acid of the nitrating process in a form suitable for its return to the process. The practical importance of the recovery may be estimated from the following table, which exhibits the amount of nitric acid used for the production of 1 ton of T.N.T. and illustrates the continued improvement of the recovery:

June, 1917 (no recovery)	1·27 tons
December, 1917	1·19 ,,
June, 1918	1·05 ,,
September, 1918	0·955 ,,

Without recovery, one-third more acid was required per ton of manufactured product than with effective recovery.

The first section of the recovery plant [which in the lecture was illustrated by numerous slides] consisted of denitrators, various types of which were tested, that finally adopted being on the principle of a rectifying still. Each denitrator was constructed of acid-resisting brick, was square in section, and was divided into six compartments by finely perforated earthenware plates (malting tiles), through each of which passed a wide overflow pipe dipping into the acid of the section beneath. The waste acid from the settling tanks was fed to the topmost section, and the denitration was effected by steam introduced into the lowest section. The steam passed upwards through the small perforations, and thus bubbled through the acid lying on the plates, heating and diluting it and depriving it of the nitric acid and nitrous compounds which it contained. The acid as it accumulated on each plate flowed downwards through the wide overflow pipe. No air was used in the denitration. Three units were employed, which together recovered 2 tons of nitric acid per day. The average percentage composition of the waste acid entering and leaving the denitrator was as follows:

	Sulphuric acid.	Inorganic nitrogen, calculated as nitric acid.
Waste acid	69·8	5·34
Denitrated acid	66·3	0·1 (maximum)

The denitrated acid passed to sulphuric acid concentrators, and the gases from the denitrators to silica cooling spirals, which con-

densed the issuing steam and nitric acid to a dilute nitric acid solution, afterwards fed to the recovery towers. The cooled, uncondensed nitrous gases passed into wide earthenware mains, in which they were mixed with excess of air. The mixture was then led into a large brickwork chamber to afford time for oxidation to take place. Thence the gases passed to a series of six recovery towers, 90 cm. in diameter and 5 m. high, packed with earthenware rings to secure proper distribution of liquid and gas. In each tower the gas entered below and met the descending liquid. The solution withdrawn at the foot was raised by means of Pohle air-lifts to a distributing vessel at a level above the top of the towers. From this the solution could be passed once more down the same tower, or on to the next tower of the series, in any proportions that might be desired.

This arrangement conferred a flexibility on the plant which was found useful. What strikes an academic chemist when he first comes into contact with works plant is its rigidity. He is accustomed to adaptable glass and rubber, and meets with inflexible metal and earthenware. A plant is usually designed on the assumption that the process will always go right—an assumption by no means well founded. Occasionally things go wrong, or a variation has to be made in the mode of working; then the rigidity of the plant shows its undesirable features. Alternative connexions may often without difficulty be introduced to obviate this, and even glass and rubber may find suitable employment on a works scale.

The series of towers was worked on the counter-current principle, the nearly exhausted gas coming into contact in the last tower of the series with dilute nitric acid from the denitrator condensers, to which water was added as required. The total free volume of the towers with their wide connecting pipes was about 28 cu. metres, and the time occupied by the gas in passing through the series was about five minutes.* Induced draught secured the steady flow of gas through the system. Cooling the liquids (and consequently the gases) as far as possible was of prime importance in the recovery, and this was largely effected in the air-lifts. The issuing gas contained 8 to 10 per cent. of oxygen.* The nitric acid solution obtained at the base of the first tower varied between 54 and 62 per cent., in accordance with the requirements of the nitration process, to which it was returned. The recovery by means of this system of denitrators and towers was more than

* Compare an article on "The Theory of Absorption Towers for Nitric Acid Manufacture," by J. R. Partington and L. H. Parker (*J. Soc. Chem. Ind.* 1919, **38**, 75).

93 per cent. of the inorganic nitrogen delivered to the denitrators in the waste acid.

The following table shows the destination of the nitrogen supplied to the T.N.T. plant as sodium nitrate, the figures being for the month of September, 1918:

Loss in nitrate bags, handling, etc. ...	0·98 per cent.
Loss in manufacture of nitric acid ...	5·42 „ „
Loss in nitration, washing, and packing...	9·91 „ „
Loss in denitration	2·03 „ „
Total loss ...	18·34 per cent.
Sent out in T.N.T. ...	81·66 „ „
	100·00 per cent.

We were greatly pleased to receive in November, 1918, communications from the Department of Explosives Supply stating that the figures in nitrogen economy during the two months of September and October constituted a record for the country, and asking us to congratulate the staff on the result, in which connexion I especially desire to mention the name of the Chief Chemist at Craigleith, Mr. Donald Grant. The figures quoted by no means exhausted the possibilities of economy, and it is certain that if the production had continued, an immediate further saving of at least 2 per cent. would have been effected, the alterations on plant necessary to secure this being practically ready at the date of the armistice.

If I may draw a moral for the academic chemist from our experience, it is that he need not fear to enter chemical industry provided he has common sense, energy, a competent knowledge of his subject, and a willingness to co-operate with engineers and men of technical experience. These qualities suffice for any chemical routine manufacture, and if he is possessed, in addition, of far-sightedness and a spark of imagination, he may, I think, venture with confidence on novel methods and new chemical industries. I am, of course, only speaking of the manufacturing side of the problem; the business side is of equal or greater importance. In Edinburgh we had no commercial difficulties; our supplies and our market were alike assured. Business training and collaboration with business men is on the part of the directing chemist essential if the enterprise is to be a commercial success.

There is, I think, at the moment a current, or perhaps an undercurrent, of belief that with the establishment of research laboratories in connexion with the various industries of this country all will necessarily be well with those industries. This opinion I do not share. Research laboratories, although indispensable, are not

in themselves sufficient to secure success in the chemical or any other manufacture. The admirable research laboratories of the German chemical works should, to my mind, be regarded rather as a noteworthy feature of the general excellence of German scientific business organisation than as the prime cause of success of the German chemical industry.

XLVIII.—*The Influence of Position on the Boiling Points of Isomeric Benzene Derivatives*

By Nevil Vincent Sidgwick.

In a previous paper (Sidgwick, Spurrell, and Davies, T., 1915, **107**, 1202) it was shown that whilst the curves of solubility in water of the three cresols, and similarly (above their triple points) those of the three toluic acids, lie very close together, the relations are quite different with the three nitrophenols, the ortho-compound being far less soluble than either of the other two, the solubilities of which are almost identical. It was suggested that this might be due to some intramolecular rearrangement taking place either in the ortho- or in the meta- and para-nitrophenols, so that they are not really all of the same type; since the behaviour of the cresols and the toluic acids showed that, where such rearrangement is impossible, or at least improbable, the influence of position on the solubility is very small. It was further pointed out that this abnormality of the nitrophenols extends also to the boiling point, the ortho-compound boiling some 80° lower than the para-, whereas the normal difference in boiling point between position-isomerides does not exceed a few degrees. It is remarkable that it is the more volatile compound which is the least soluble in water, although one would expect the reverse to be the case.

It is obviously of interest to inquire how far this abnormality of behaviour, with respect to solubility and vapour pressure, extends, and especially to determine how its occurrence is related to the chemical nature of the substituent groups. As regards the solubility, the data afforded by the literature give comparatively little assistance; but the boiling points have been recorded for a large number of benzene derivatives, and their examination leads to results of some interest.

In order to avoid error due to unconscious selection, all the boiling points of di- and poly-derivatives of benzene given in the

last edition of Richter's "Lexikon" were collected and classified according to the chemical nature of the substituents. Their use is considerably restricted by the absence of any agreement among chemists as to the pressure (other than atmospheric) at which boiling points should be observed, and the impossibility of applying any temperature-correction amounting to more than a few degrees. Even so, there remain some 500 sets of isomerides the boiling points of which are recorded under comparable conditions. The numbers are, of course, liable to considerable errors; the temperatures are frequently uncorrected, often the isomerides have been examined by different observers at different times, and it is likely that in some few instances much larger errors may have been introduced by the incorrect identification of the compounds investigated.

In spite of these difficulties, the analysis of the data shows in a sufficiently striking manner that the differences in the boiling points of isomeric derivatives vary over a wide range, and that their magnitude is closely related to the chemical nature of the substituent groups.

The simplest way of expressing the results is by means of the "greatest difference," that is, the largest difference in degrees between the boiling points (under the same pressure) of any two of the three isomerides. Taking the substituents which are least likely to undergo rearrangement—the alkyl and alkylene groups—it is found that among the di-derivatives, out of fourteen examples, the maximum value of the greatest difference is 19° and the mean 7·6°, or, excluding two instances, the maximum is 13° and the mean 5·8°. Among the tri-derivatives, we find: out of 7, maximum 18°, mean 7·0°, or, excluding one, maximum 11°, mean 5·2°.

We may therefore assume that a change in the position of an alkyl group does not alter the boiling point by more than 10°. This enables us to extend the basis of our induction by including those tri-derivatives in which one at least of the substituents is an alkyl or alkylene group, since the position of this group will have little effect on the boiling point.

The following tables are drawn up on this principle. In table I the two substituents are given first, then the number of sets of isomerides coming under this head, then the maximum and mean values of the "greatest differences" in boiling point. This is then given for the tri-derivatives, it being understood that the third substituent is always an alkyl group. When two sets of figures are given under one heading, the second is arrived at by excluding one or two extreme values, as being probably due to experimental error. In table II the results for the di-derivatives are summarised, the mean values alone being quoted. In this table a class of com-

pounds with two different substituents occurs twice, once under each of its two groups.

The abbreviations mostly explain themselves. "Alk." stands for an alkyl or alkylene group; "NHX" for an amine group with one substituent other than an alkyl.

TABLE I.

Substituents.	Di-derivatives. No.	Max.	Mean.	Tri-derivatives. No.	Max.	Mean.
Alk. : Alk.	14	19°	7·6°	7	18°	7·0°
	12	13	5·8	6	11	5·2
Alk. : Ester	8	22	8·1	3	11	5·0
	7	10	6·0	—	—	—
Alk. : Ether	25	23	7·9	6	23	11·5
	24	11	7·3	4	12	6·0
Alk. : Halogen	12	14	6·3	13	11	6·3
Alk. : CH	6	15	10·0	4	13	9·2
Alk. : C_nH_{2n}·OH	3	7	6·0	2	13	9·0
Alk. : SH	1	—	2·0	2	5	3·5
Alk. : NH_2	6	10	5·2	2	14	13·0
Alk. : C_nH_{2n}·NH_2	3	10	4·0	—	—	—
Alk. : NHAlk.	4	5	3·4	2	14	12·0
Alk. : NHX	7	12	9·3	—	—	—
Alk. : CN	3	14	6·0	2	13	9·5
Alk. : CHO	1	—	5·0	1	—	10·0
Alk. : OAcyl	4	9	6·5	2	9	8·5
Total	98	23	6·85	45	23	8·2
	94	15	6·3	42	14	7·3
Alk. : NO_2	3	26	20·3	2	48	44·0
Alk. : $NAlk_2$	2	32	27·0	1	—	36·0
Alk. : CO·Alk	2	19	15·5	6	25	12·0
Alk. : CO_2H	1	—	15·0	1	—	8·0
Alk. : CO·$N(CH_3)_2$	1	—	37·0	—	—	—
Aryl : Halogen	2	14	13·5	—	—	—
Aryl : OH	1	—	33·0	—	—	—
Aryl : NH_2	1	—	48·0	—	—	—
OAlk. : OAlk	6	17	6·5	3	33	14·7
	5	9	4·4	2	11	5·5
OAlk. : Ester	6	25	16·0	4	15	9·0
OAlk. : Halogen	8	13	17·6	1	—	32·0
OAlk. : OH	2	39	34·5	5	26	15·8
OAlk. : C_nH_{2n}·OH	4	15	12·8	1	—	7·0
OAlk. : NH_2	3	40	33·0	3	30	23·0
OAlk. : CN	2	12	6·0	—	—	—
OAlk. : CHO	2	18	14·5	4	17	9·5
OAlk. : OAcyl	2	17	11·0	—	—	—
OAlk. : NO_2	2	19	13·5	2	30	19·7
OAlk. : CO·Alk	3	18	12·3	5	18	8·2
Ester : Ester	2	17	9·0	—	—	—
Ester : Halogen	4	15	7·5	—	—	—
Ester : OH	2	66	33·0	2	59	33·5
Ester : NH_2	1	—	30·0	—	—	—
Halogen : Halogen	2	17	9·0	4	29	14·0
	—	—	—	3	12	9·0

TABLE I. (*continued*).

Substituents.	Di-derivatives. No.	Max.	Mean.	Tri-derivatives. No.	Max.	Mean.
Halogen : CH_2·OH ...	1	—	7·0	—	—	—
Halogen : OH	2	44	43·5	2	44	42·0
Halogen : NH_2	2	26	13·0	2	22	19·5
Halogen : NHAlk.......	1	—	24·0	—	—	—
Halogen : NHAcyl ...	2	30	25·0	—	—	—
Halogen : $NAlk_2$	2	27	26·0	—	—	—
Halogen : NO_2	3	7	5·3	2	25	19·0
Halogen : CHO	2	10	7·5	—	—	—
Halogen : COCl	3	24	15·7	—	—	—
Halogen : CN	2	27	17·5	—	—	—
OH : OH	1	—	34·0	1	—	36·0
OH : NO_2	1	—	80·0	—	—	—
OH : CHO	1	—	43·0	1	—	20·0
OH : CO·CH_3...........	—	—	—	1	—	68·0
NH_2 : NH_2	1	—	26·0	1	—	29·0
NH_2 : NHAlk.	2	27	23·5	2	13	11·5
NH_2 : $NAlk_2$	2	51	33·0	1	—	24·0
NH_2 : CO·Alk.	1	—	47·0	—	—	—
NH_2 : CN	1	—	24·0	—	—	—
NHAlk. : NHAlk.	1	—	29·0	—	—	—
NHAlk. : $NAlk_2$.........	1	—	15·0	—	—	—
$NAlk_2$: $NAlk_2$	1	—	50·0	1	—	32·0
NO_2 : NO_2	1	—	19·0	—	—	—
NO_2 : CO·Alk...........	1	—	20·0	—	—	—
COCl : COCl	1	—	23·0	—	—	—

Summarising these results, we find that the compounds may be divided into three groups.

I. *Difference of Boiling Points less than* 10°.—These may be called the normal compounds. They include the following substituents: alkyl groups alone, or one or more alkyls with an ester, alkyloxy-, alcohol, halogen, aldehyde, amino-, monoalkylamino-, or hydroxyl group; also two alkyloxy- or one alkyloxy- and one halogen, two halogens, or one halogen with one ester or nitro- or aldehyde or ketone group.

II. *Difference*, 10—20°.—This group includes alkyl + carboxyl or ketone, and alkyloxy- + alcohol, ester, aldehyde, ketone, or nitro-.

III. *Difference*, 20—80°.—Abnormal compounds. These are: alkyl + dialkylamino-, dialkylamido-, or nitro-; alkyloxy- + amino- or hydroxyl; halogen + alkylamino-, dialkylamino-, acylamino-, and hydroxyl; amino-esters and hydroxy-esters; all derivatives containing an amino- or hydroxy-group with any substituent other than alkyl.

TABLE II.

Summary.

	Alkyl.	CN.	O·Acyl.	SH.	$C_nH_{2n}\cdot OH$.	$C_nH_{2n}\cdot NH_2$.	O·Alk.	Halogen.	CO_2H.	CO_2Alk.	CHO.	CO·Alk.	COCl.	NHAlk.	NH·Acyl, etc.	NH_2.	$NAlk_2$.	$CO\cdot NAlk_2$.	NO_2.	Aryl.	OH.
Alkyl	5·6	6·0	6·5	2·0	6·0	4·0	7·3	6·3	15·0	6·0	5·0	15·5	—	3·4	9·3	5·2	27·0	37·0	20·3	—	6·0
CN	6·0	—	—	—	—	—	6·0	17·5	—	—	—	—	—	—	—	—	—	—	—	—	—
OAcyl	6·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SH	2·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$C_nH_{2n}\cdot OH$	6·0	—	—	—	—	—	12·8	7·0	—	—	—	—	—	—	—	—	—	—	—	—	—
$C_nH_{2n}NH_2$	4·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
OAlk.	7·3	6·0	—	—	12·8	—	6·5	7·6	—	16·0	14·5	12·3	—	—	—	33·0	—	—	13·5	—	34·5
Halogen	6·3	17·5	—	—	7·0	—	7·6	5·2	—	7·5	7·5	—	16·0	24·0	25·0	13·0	26·0	—	4·0	13·5	43·5
CO_2H	15·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$CO_2\cdot Alk$	6·0	—	—	—	—	—	16·0	7·5	—	9·0	—	—	—	—	—	30·0	—	—	—	—	33·0
CHO	5·0	—	—	—	—	—	14·5	7·5	—	—	—	—	—	—	—	—	—	—	—	—	43·0
CO·Alk.	15·5	—	—	—	—	—	12·3	—	—	—	—	—	—	—	—	—	—	—	20·0	—	—
COCl	—	—	—	—	—	—	—	16·0	—	—	—	—	23·0	—	—	—	—	—	—	—	—
NHAlk.	3·4	—	—	—	—	—	—	24·0	—	—	—	—	—	29·0	26·0	—	—	—	—	—	—
NHAcyl	9·3	—	—	—	—	—	—	25·0	—	—	—	—	—	—	—	—	—	—	—	—	—
NH_2	5·2	—	—	—	—	—	33·0	13·0	—	30·0	—	—	—	28·0	26·0	—	—	—	—	48·0	—
$NAlk_2$	27·0	—	—	—	—	—	—	26·0	—	—	—	—	—	—	—	50·0	—	—	—	—	—
$CO\cdot NAlk_2$	37·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NO_2	20·3	—	—	—	—	—	13·5	4·0	—	—	—	20·0	—	—	—	—	—	—	19·0	—	80·0
Aryl	—	—	—	—	—	—	—	13·5	—	—	—	—	—	—	48·0	—	—	—	—	—	33·0
OH	6·0	—	—	—	—	—	34·5	43·5	—	33·0	43·0	—	—	—	—	—	—	—	80·0	33·0	34·0
Means:	10·2	9·8	6·5	2·0	8·6	4·0	14·9	16·2	15·0	16·9	17·5	19·3	19·5	18·1	17·2	22·2	34·7	37·0	26·1	31·5	39·1

It is to be noticed that the abnormality of the hydroxy- and amino-derivatives does not extend to those in which these groups are attached to a side-chain, as in the aromatic alcohols and benzylamine compounds; also, whilst a halogen, amino-, or hydroxy- with an *alkyl* group gives a normal compound, the analogous compounds with an *aryl* group instead of an alkyl (diphenyl derivatives) are, so far as they are known, highly abnormal.

The general impression conveyed by these results is that the property is not an additive one for the two substituents, but rather that it depends on the interaction of the two. This is shown, for example, in the behaviour of the halogens and the nitro-group, which with themselves or one another give normal compounds, whereas in conjunction with other groups, especially in amines or phenols, they cause great abnormality.

When we come to the order of the boiling points of the ortho-, meta-, and para-compounds, it is clear that the discussion of the normal compounds, where the differences are small, requires data more exact than many of those on which the foregoing tables are based. Among the abnormal compounds, on the other hand, the differences are large enough for trustworthy conclusions to be drawn from them. The general conclusion is that in the abnormal group the ortho- have by far the lowest boiling points, and the meta- and para- do not differ greatly, but the meta- nearly always have rather lower boiling points than the para-. This relation is supported, so far as concerns the phenol derivatives, by the solubilities in water, where the meta- and para- in all instances hitherto examined give very similar curves, whilst that of the ortho- is quite different. It is particularly remarkable that the ortho-compound, with the highest vapour pressure, is the least soluble in water.

*There are, however, some exceptions to these rules as to the boiling points.** COCl:COCl, b. p. *o*-, 281°, *m*-, 276°, *p*-, 259°. This is entirely anomalous. The high boiling point of the ortho-compound may be due to the substance having the ring formula, as has already been suggested on chemical grounds; but, if so, the equally high boiling point of the meta-derivative would seem to point to a ring structure for this as well; also in the compounds Br:CN and NO_2:NO_2 the ortho-compound has a much higher boiling point than the other two.

Comparing the meta- and para-isomerides, we find that the para- has the higher boiling point in all but twelve cases. Excluding one of these, in which the difference is only 1° and may be due to experimental error, all the other eleven without exception contain one or two amino- or substituted amino-groups (CH_3:NMe_2,

* These compounds are conveniently described by means of the two substituents alone.

$CH_3:NEt_2$, $CH_3 \cdot O:NH_2$, $Cl:NMe_2$, $NMe_2:NMe_2$, and NH_2 with NH_2, NHMe, NHEt, NMe_2, and NEt_2). This indicates some constitutional peculiarity which needs explanation.

The measurements given in the following paper of the vapour pressures of substituted benzoic acids at 100° enable the conclusions to be extended to these classes of compounds. It will be seen that the vapour pressures of the toluic acids, which are slightly abnormal, having a difference of boiling point of 15·5°, vary in the ratio of 4·5 : 1. The chlorobenzoic acids have about the same ratio. In the nitrobenzoic acids the difference is distinctly larger (20 : 1), and in the hydroxybenzoic and hydroxytoluio acids it is enormous (1300 : 1 and 300 : 1). It thus appears that whilst the compounds $CH:CO_2H$ and $Cl:CO_2H$ are almost normal, $NO_2:CO_2H$ is markedly abnormal, and $OH:CO_2H$ more so than any other compound yet examined. It will also be noticed that in these last two groups the ortho-compound is always the most, and the para- the least, volatile.

Summary.

With regard to the influence of position on the boiling point, the derivatives of benzene may be divided into two classes, namely, normal and abnormal.

(1) The normal derivatives are those in which the influence is small, the difference of boiling point seldom exceeding 10° for any set of isomerides. In this class the substituents are, as a rule, of an unchangeable type, such as alkyl (not aryl), or alkyloxy-, or ester groups. When all but one of the substituents are alkyl groups, the compound is almost always normal.

(2) Abnormal derivatives are those in which the boiling points differ by more than 10°, usually from 20° to 80°, the boiling points of the meta- and para- being near to one another, whilst that of the ortho- is much lower. In these compounds the substituents are of a reactive character. If a substance contains two reactive groups and, say, an alkyl, a change in the relative positions of the two reactive groups has a large effect on the boiling point; but a change in the position of the alkyl has only a small one.

These relations extend to the solubilities in water, so far as they have been observed. Normal compounds show similar solubilities; in abnormal compounds, the solubilities are very different, and when one of the substituents is a hydroxyl, the ortho-compound (in spite of its higher vapour pressure) is far less soluble in water than the meta- and para-, the solubilities of which, like their boiling points, lie close together.

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XLIX.—*Volatility in Steam: Benzoic Acid and its Derivatives.*

By Nevil Vincent Sidgwick.

Considering the technical importance of steam distillation, it is remarkable that it has been the subject of comparatively few scientific investigations. The volatility or otherwise of an organic substance in steam is one of the most familiar properties in organic chemistry, but only in a small number of instances (see Naumann, *Ber.*, 1877, **10**, 1421, 1819, 2014, 2099; Naumann and Müller, *Ber.*, 1901, **34**, 224; Ryland, *Amer. Chem. J.*, 1899, **22**, 384; Charabot and Rocherolles, *Bull. Soc. chim.*, 1904, [iii], **34**, 533; Richmond, *Analyst*, 1908, **33**, 209, 305; 1917, **42**, 125, 133; Stein, *J. pr. Chem.*, 1913, [ii], **88**, 83) have any attempts been made to determine it quantitatively.

Partly on account of the general interest of this property, and partly with the view of extending the data given in the preceding paper as to the influence of position on volatility to substances which decompose below their boiling points, I have been led to examine this subject, and in this paper an apparatus is described by which the volatility in steam of a substance from its saturated aqueous solution can readily be determined with an accuracy of 1 or 2 per cent. with quite a small quantity of material, and the results obtained with benzoic acid and a series of its derivatives are discussed.

In the distillate obtained under these conditions, the weights of the components are in the ratio of the products of their molecular weights into their partial pressures in the vapour. When they are immiscible, these partial pressures will be the vapour pressures of the pure components at the temperature of the distillation, where the total pressure is one atmosphere.

If any two vapour-pressure curves are compared, it will practically always be found (invariably if the boiling points of the two substances lie far apart) that as the temperature rises the ratio of the pressures approaches unity. Thus for ether and water the ratio at 0° is 40·4, and at 80° is 8·37; for benzoic acid and water it is 0·00220 at 100° and 0·0260 at 249°. The reason for this is easily seen. The change of vapour pressure with temperature is approximately given by the equation

$$\log p = A - \frac{B}{T},$$

where p is the vapour pressure at the absolute temperature T, and A and B are constants depending on the substance. For water in the neighbourhood of 100°, $A = 8{\cdot}66$ and $B = 2156$. For organic substances boiling above 100°, A varies within rather narrow limits, lying nearly always between 7·5 and 10, and usually between 8 and 9. The result is that if $\log p$ is plotted against $1/T$ for any number of substances, a series of straight lines is obtained radiating from points on the $\log p$ axis (where $1/T = 0$, and hence $\log p = A$) which lie close together; that is, the lines all approach one another as the temperature rises. The distance between any two lines on this diagram, however, is equal to the difference of logarithms of the pressures of the two substances, that is, is the logarithm of the ratio of their vapour pressures. Hence, as the temperature rises, the value of $\log (p_1/p_2)$ approaches zero, and the ratio p_1/p_2 approaches unity.* It follows that in the process of steam distillation, where the object is always to get the maximum proportion of a substance of higher boiling point than water in the distillate, the efficiency is greater the higher the temperature or the greater the pressure at which the distillation is carried out. This fact has been recognised in technical practice, although the reason has not hitherto been stated.

If the substance is perceptibly soluble, it will lower the vapour pressure of the water; the distillation will take place at a higher temperature, and the proportion of the substance in the distillate will be increased. With most of the substances dealt with in this paper, the influence of this factor is small; it is also easily allowed for if the temperature of the liquid is known. In dealing with the effect of solubility on the partial pressure of the other component, the substance A, two cases have to be distinguished, that in which it is solid and that in which it forms a second liquid layer. If the substance is solid, its partial pressure in the vapour from the saturated solution is equal to the vapour of the solid substance at the temperature of the distillation. This method, in fact, offers the simplest means of measuring the vapour pressure of a solid at 100° down to values of the order of a thousandth of a mm. (or even lower if sufficiently accurate analytical methods are available). For the purpose of comparison, however, it is more important to know the vapour pressure in the liquid than in the solid state. As was pointed out in discussing the solubilities of the toluic acids (T., 1915, **107**, 1209), the regularities observed in liquid–liquid systems disappear when the solid phase is formed, owing, no doubt,

* Charabot and Rocherolles (*loc. cit.*) laid down the rule that the ratio of organic substance to water in the distillate always approaches unity as the temperature rises; but this is obviously not always true.

to the effect of the crystallographic forces, which is most clearly shown in the wide divergences in melting point of otherwise similar substances. The vapour pressure of a solid is necessarily less than that of the (supercooled) liquid at the same temperature, and the more so the further that temperature is removed from the melting point. The relation between the two can be calculated if the heat of fusion is known, for it can be shown that if p, p' are the vapour pressures of the substance in the liquid and solid states at a temperature T (absolute) below its melting point T_0, and if W is the molecular heat of fusion in calories, then

$$2{\cdot}3026 \log \frac{p}{p'} = \frac{W}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where $R = 1{\cdot}985$.

As an example of the influence of this factor, we may take *p*-toluic acid (m. p. 177°). Its heat of fusion is not exactly known, but it may be taken to be of the order of 5000 cals. per gram-molecule. At 100° we have

$$2{\cdot}3026 \log \frac{p}{p'} = \frac{5000}{1{\cdot}985}\left(\frac{1}{373} - \frac{1}{450}\right)$$

whence $\log p/p' = 0{\cdot}5019$ and $p/p' = 3{\cdot}17$. The observed vapour pressure of the solid acid at 100° is 0·216 mm. It follows that that of the liquid at 100° would be $0{\cdot}216 \times 3{\cdot}17 = 0{\cdot}685$ mm., which is very near to the values for the *ortho*- (0·970) and *meta*- (0·607) acids, which are liquid under water at 100°. These calculations are not worth discussing in more detail until the heats of fusion of the acids in question have been measured with greater accuracy, which is now being done.

When the substance forms a second liquid layer, the vapour pressure which is being measured is the partial pressure of the substance in the vapour in equilibrium with either of the two liquid phases (since the same vapour must be in equilibrium with both). If we consider the phase richer in A, it is obvious that p_A will be lowered by the presence of dissolved water. It will be less than the vapour pressure of pure liquid A, and also less than that of solid A. It is difficult to calculate how much it is diminished, because binary liquids in the neighbourhood of the point at which they separate into two liquid layers depart widely from the simple solution laws. It may, however, be pointed out that in the case, for example, of *m*-toluic acid (m. p. 110·5°; triple point with water 91·8°), the liquid at the triple point, where the partial pressure of the acid in the vapour is equal to the vapour of the solid acid, contains 44·2 molecules per cent. of water, whilst

at 100° the acid layer contains 49·8 molecules per cent. Assuming the vapour-pressure law, we should expect the extra 5·6 molecules per cent. of water to lower the vapour pressure of the acid by the same percentage, or less if the acid is associated in the liquid to a smaller degree than the water, and this may be taken as giving a rough idea of the magnitude of the effect. Young ("Fractional Distillation," 1903, p. 92) found that at atmospheric pressure the amount of aniline in the distillate from a mixture of aniline and water was 14 per cent. less than that calculated from the vapour pressures of the pure components, and at this temperature the aniline dissolves about 35 molecules per cent. of water. With benzoic acid the vapour pressure of the pure liquid has been measured by Kahlbaum (*Zeitsch. physikal. Chem.*, 1898, **26**, 603) down to 132·5°, where it is 10 mm. By extrapolation, using the logarithmic formula, it is found to be 1·67 mm. at 100°. Its heat of fusion is 4830 cals. (Ciamician and Garelli, *Zeitsch. physikal. Chem.*, 1895, **18**, 54), and its melting point 122·7°. Hence the vapour pressure of the solid acid at 100° is 1·15 mm. As the triple point is only 5° lower, we should not expect the partial pressure of the acid in the vapour at 100° to be much lower than that of the solid acid at the same temperature. It was actually found by the steam distillation method to be 1·129 mm., a difference of only 2 per cent.

EXPERIMENTAL.

A series of preliminary experiments with a pure sample of benzoic acid showed that the steam became saturated with the acid when it had passed through two small flasks containing a mixture of the acid and water, but that it was essential to avoid recondensation of the vapour after it had left the liquid, as this always gave low results, owing no doubt to the fact that the volatility is less at lower temperatures. The form of apparatus finally adopted was as follows. The acid was contained in two 120 c.c. flasks with short, wide necks. Steam from a boiler was passed through a trap to catch water-drops, and was led to the bottom of the first flask and thence by a short bent tube to the bottom of the second. From this it passed through a Kjeldahl trap to the condenser. The cork of the second flask carried a thermometer graduated in fifths of a degree, with its bulb reaching nearly to the bottom of the flask. The flasks were immersed up to their necks in a glycerol-bath, which was kept a few degrees above the temperature of the distillation, and the whole of the apparatus above the glycerol was carefully lagged—the tube from the steam-trap to the first flask and that connecting the two flasks being wrapped in felt, and

the Kjeldahl-trap surrounded by a jacket moulded on to it from asbestos millboard and dried. This was cut into two halves, so that it could be removed for cleaning the trap. The amount of acid in each flask was from 3 to 20 grams (according to the solubility), and the steam was passed at a rate of 2—4 grams per minute. With this apparatus it was found that, although the first fraction of the distillate gave a low value, subsequent fractions were of constant composition, as is shown by the following two experiments (the successive fractions were from 70 to 150 c.c. each; the numbers give the percentage of acid in the distillate): Expt. I: 0·90, 1·004, 0·994, 0·980, 0·984. Expt. II: 0·89, 1·004, 0·981, 1·000, 1·018.

The results obtained on any one day were found to agree better among themselves than the means of different days did with one another. This was traced to changes in the barometric pressure. From Kahlbaum's measurements (*loc. cit.*) of the vapour pressure of benzoic acid, *R*, the ratio of its vapour pressure to that of water can be calculated at a series of temperatures in the neighbourhood of 100°. It is found that *R* increases for 1° rise of temperature by 2·76 per cent., or, since an increase of pressure of 27·4 mm. raises the boiling point of water by 1°, 1 mm. rise of the barometer will increase the proportion of acid in the distillate by 0·101 per cent. of its value, which is quite an appreciable amount. The following table shows the results obtained when this correction is applied. The four experiments were carried out on different days. The value given for the percentage of acid in the distillate is in each case the mean of the titrations of from three to six different fractions. The numbers under "correction" are the amounts which must be added to give the true composition of the distillate under 760 mm. pressure.

Expt.	Pressure.	Weight-percentage of acid in distillate.	Correction.	Corrected percentage.
D	745·0	0·987	+0·015	1·002
E	750·2	0·991	+0·010	1·001
F	750·2	0·999	+0·010	1·009
G	755·5	1·006	+0·004	1·010
			Mean......	1·006

To prove that the vapour was saturated with acid, the distillation was repeated under the same conditions, except that the steam was not generated from water alone, but from a mixture of 800 c.c. of water and 80 grams of pure benzoic acid. In this way, saturation must be attained. It was difficult to secure a steady flow of steam, as the two layers in the flask made the liquid boil irregularly, and this might be expected to give a slightly low value, as any

interruption of the distillation leads to some re-condensation of the vapour. The mean value so obtained was 0·984 per cent. at 750·4 mm., corresponding with 0·994 at 760 mm. This is 1·2 per cent. below the mean of the other four experiments, which are doubtless more trustworthy, for the reason mentioned, but it is enough to show that the apparatus secures complete equilibrium between the solution and the vapour.

With the other acids examined, the measurements were made in less detail, and only the final means are quoted; these are always the means of the concordant titrations of at least three different fractions of distillate. The accuracy naturally varies with the nature of the acid. When this melts under water below 100° there is little difficulty. When it remains solid, it is not easy to remove it completely from the condenser, although this can generally be done by running out the water. It may be assumed that the mean results are within 2 or 3 per cent. of the truth in all cases, except where (as with *p*-hydroxybenzoic acid) the amount of acid in the distillate is too small for accurate titration.

The acids used were in most instances laboratory specimens purified by recrystallisation. I am greatly indebted to Miss E. Ewbank for her kind assistance in the preparation of some of these acids and in the purification of others.

The preparation and behaviour of the individual acids may be briefly described as follows. (Acids marked with an asterisk are liquid under water at 100°.) The solubility data, where no other reference is given, are derived partly from unpublished measurements made by Miss Ewbank in this laboratory and partly from the work of Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien.*, 1909, **118**, II*b*, 695). The solubilities are expressed in grams of acid in 100 grams of solution.

Benzoic Acid.*—A specially pure sample free from chlorine: purified by recrystallisation. M. p. 122·7°. Triple point with water, 95°. Solubility in water at 100°, 8·0 per cent. (Alexéev, *Ann. Phys. Chem.*, 1888, [iii], **28, 305.)

**Phenylacetic Acid.*—Pure laboratory specimen. M. p. 76·7°. Triple point, 46·5°. Solubility at 100°, 11·2 per cent.

**β-Phenylpropionic Acid.*—Recrystallised from light petroleum. M. p. 48·6°. Triple point, 34·0°. Solubility at 100°, 3·5 per cent.

Toluic Acids.†—Recrystallised from water.

	M. p.	Triple point.	Solubility.
*Ortho	102·4°	93·5°	2·97 per cent.
*Meta	110·5	91·8	1·98 ,,
Para	176·8	(142·0)	1·16 ,,

† Solubility data: Sidgwick, Spurrell and Davies, T., 1915, **107**, 1207. I take this opportunity of expressing my regret that when this paper was

Hydroxybenzoic Acids.—Recrystallised from water until their melting points and solubilities in water were not further changed. All these acids remain solid. The value given in the table for the volatility of the para-acid is only approximate. One drop of $N/10$-alkali was more than sufficient to neutralise the acid in 100 c.c. of distillate, and as the acid cannot be sharply titrated, it did not seem worth while to use $N/100$-alkali.

	M. p.	Solubility at 100°.
Ortho	159·0°	6·45 per cent.
Meta	201·3	36·9 ,,
Para	213·0	33·5 ,,

Hydroxytoluic Acids.—The acids $CH_3:CO_2H:OH = 1:3:2$, 1 : 4 : 3, and 1 : 3 : 4 were obtained from the technical cresotic acids by distillation in steam and recrystallisation. The 1 : 3 : 6-acid was boiled with animal charcoal and recrystallised from alcohol and water. The 1 : 4 : 2-acid was prepared by the sulphonation of *p*-toluic acid and fusion of the product with alkali (Perkin and Meldrum, T., 1908, **93**, 1419). It was purified by recrystallisation from water.

$CO_2H:OH:CH_3$.*	M.p.	Triple point.	Solubility at 100°.
1 : 2 : 3	167·0°	(129·0°)	1·16 per cent.
1 : 2 : 4	177·8	(131·0)	0·94 ,,
1 : 2 : 5	152·5	(107·8)	2·15 ,,
1 : 3 : 4	172·4	—	4·36 ,,
1 : 4 : 3	207·0	—	5·25 ,,

Nitrobenzoic Acids.—The ortho-acid was purified through the barium salt (Holleman, *Rec. trav. chim.*, 1898, **17**, 247). The behaviour of this acid was quite peculiar. It gives with water an unbroken solubility curve up to its melting point without a two-liquid portion. This curve, like that of salicylic acid, is very flat in the middle, that is, the solubility increases very greatly for a small rise of temperature. For example, at 78° it is 20 per cent. and at 82° it is 70 per cent. In the distillation, it was found impossible to get the acid to remain solid in the presence of steam. It melted at once, forming a homogeneous liquid. Its temperature varied with that of the glycerol-bath, remaining some 8—12° below it. Finally, a series of fractions were taken at 117° (bath, 123—126°), which gave concordant titrations.

The most probable explanation of this behaviour (which was not observed with any other acid) is that the vapour-pressure curve of

published we were unaware of the paper by Flaschner and Rankin quoted above, in which the solubilities of the toluic acids in water are given. Our results are in substantial agreement with theirs.

* The substituents are arranged in the order of their influence on the volatility.

the saturated solution (which with any substance giving an unbroken solubility curve must rise with the temperature to a maximum and then fall to the vapour pressure of the pure substance at its melting point) never attains the value of one atmosphere. If so, the solution which the acid forms in contact with steam at one atmosphere, since it must have a vapour pressure of 760 mm., must be somewhat unsaturated, and both the composition of this solution and the partial pressure of the acid will vary with the temperature.

The meta- and para-acids were purified by recrystallisation.

	M. p.	Triple point.	Solubility at 100°.
Ortho	146·8°	—	92·8 (at 117°)
*Meta	141·4	76·8°	10·5
Para	242·4	—	0·29

Chlorobenzoic Acids.—The ortho- and para-acids were prepared from the corresponding toluidines by Sandmeyer's reaction and purified by recrystallisation. The meta-acid was recrystallised from benzene.

	M. p.	Triple point.	Solubility at 100°.
Ortho	140·3°	(104·8°)	4·02 per cent.
Meta	154·5	(123·8)	0·5 ,,
Para	241·5	—	0·11 ,,

Determination of Temperature.—This was somewhat inaccurate, owing to the uncertain correction for the emergent stem, which was determined by conducting a distillation with nothing but water in the bulbs and varying the temperature of the bath. In the actual distillation of the acids, the thermometer readings remained steady in nearly every case to about 0·04°, but with most acids the elevation of the boiling point is so small that the readings are of no great value; they are therefore only quoted when they amount to 0·1° or more.

The results are collected in the following table. The first column gives the name of the acid; the second (dt) the elevation of the temperature above 100° (reduced to 760 mm.); the third the percentage by weight of the acid in the distillate; the fourth the partial pressure of the acid in hundredths of a mm. The latter is calculated from the formula

$$p_A = \frac{\text{Wt. of acid}}{\text{Wt. of water}} \times \frac{760 \times 18}{M},$$

where M is the molecular weight of the acid. The fifth column gives the solubility (in grams per 100 grams of solution) of the acid in water at the temperature of the distillation. The sixth gives the partition-coefficient of the acid between the vapour and

Acid.	dt.	Percentage in distillate.	Vapour pressure in mm. × 100.	Solubility.	Partition coefficient × 10⁶.	Relative Vapour pressure	Relative Partition.
Benzoic*	0·12°	1·006	112·9	8·0	73·9	1·0	1·0
Phenylacetic*	0·16	0·294	29·55	11·2	15·43	0·262	0·208
β-Phenylpropionic*	—	0·247	22·5	3·5	41·4	0·200	0·560
Toluic: *ortho**	0·10°	0·964	97·0	2·97	191·0	4·49	1·75
*meta**	—	0·604	60·7	1·98	136·0	2·81	1·25
para	—	0·215	21·6	1·16	108·9	1·0	1·0
Hydroxybenzoic: ortho	—	0·400	39·7	0·45	36·5	1320·0	6890·0
meta	1·06°	0·0015	0·149	36·9	0·024	5·0	4·53
para	0·01	0·0003	0·030	33·5	0·005	1·0	1·0
Hydroxytoluic: $CO_2H : OH : CH_3$ ortho : 3	—	0·201	23·5	1·16	132·4	326·4	1471·0
,, : 4	—	0·135	12·1	0·94	80·1	168·0	890·0
,, : 5	—	0·202	18·2	2·15	55·3	253·0	614·0
meta : 4	—	0·0196	1·76	4·36	2·64	24·4	29·3
para : 3	0·17°	0·0008	0·072	5·25	0·090	1·0	1·0
Nitrobenzoic: ortho	17·0°	0·0246	2·01	92·8	0·156	20·9	0·0655
meta*	0·10	0·0085	0·70	10·5	0·479	7·29	0·201
para	—	0·0017	0·096	0·29	2·38	1·0	1·0
Chlorobenzoic: ortho	—	0·206	18·03	4·02	30·2	4·01	0·110
meta	0·63°	0·225	19·70	0·5	260·0	4·38	0·96
para	—	0·0515	4·50	0·11	275·0	1·0	1·0

the liquid, that is, the concentration in the vapour divided by that in the saturated solution. The last two columns give the values of the vapour pressures and the partition-coefficients referred to those of the para-acid (or with the first three acids to those of benzoic acid) as unity.

Volatility and Boiling Point.

To bring these results into line with the data tabulated in the preceding paper, it would be necessary to calculate the boiling points of the acids from their vapour pressures at 100°. This can be done if we assume a value for either of the two constants A and B of the vapour-pressure formula. Such an assumption, however, is scarcely justified; where the vapour pressures are abnormal we may expect these constants to be abnormal also, but experience shows that heats of evaporation do not vary very widely, and hence a large difference in the vapour pressure at 100° may be taken to involve a large difference in boiling point.

It is more satisfactory to take as the basis of comparison the ratio of the vapour pressures of the isomerides at 100°. These values can be obtained by interpolation for those derivatives the vapour-pressure curves of which have been measured over a suitable range of temperature, and the ratios compared with those given by the substituted benzoic acids. The following table is constructed in this way. The values are relative, that for the para- (or, where that is missing, the meta-) isomeride being taken as unity. The last column gives the greatest difference in boiling

Substituents.	Relative vapour pressure at 100°. Ortho.	Meta.	Para.	Greatest difference in b. p.
$CH_3 : CH_3$	0·788	0·862	1	5·6°
$CH_3 : Cl$	1·097	0·896	1	3·0
$CH_3 : NH_2$	1·037	0·870	1	3·6
$CH_3 : OH$	1·722	1·026	1	11·0
$CH_3 : NO_2$	1·653	—	1	17·3
$Cl : NH_2$	2·277	1·0	—	19·7
$CH_3 : CO_2H$	4·49	2·81	1	15·5
$Cl : CO_2H$	4·01	4·38	1	—
$NO_2 : CO_2H$	20·9	7·3	1	—
$OH : CO_2H$	13 20·0	5·0	1	—
$CO_2H : OH : CH_3$	1 : 2 : 3 326·0	—	—	—
	1 : 2 : 4 168·0	1 : 3 : 4 24·4	1 : 4 : 3 1	—
	1 : 2 : 5 253·0	—	—	—

[1] Woringer, *Zeitsch. physikal. Chem.*, 1900, **34**, 262.
[2] Feitler, *ibid.*, 1889, **4**, 71.
[3] Kahlbaum, *ibid.*, 1898, **26**, 603.

point at 760 mm. The first three series show the behaviour of normal compounds, in the sense in which this term is used in the preceding paper; the cresols are slightly, and the last two series distinctly, abnormal. Of the acids dealt with in the present paper, the boiling points of the toluic acids only have been determined.

The vapour-pressure curves from which the data for the first six series are obtained are all, of course, those of liquids. The differences among the acids might no doubt be somewhat reduced if they were compared in the liquid state, account being taken of the difference of vapour pressure of solid and liquid at temperatures some way below the melting points; as we have seen, the ratio for the toluic acids is reduced in this way to 1·6. The extreme abnormality of the hydroxy-derivatives is very marked.

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L.—*Observations on Some Organic Compounds of Arsenic.*

By Alex. McKenzie and John Kerfoot Wood.

The following is an account of part of the work carried out in Dundee during 1918 in connexion with the Chemical Warfare Department of the Ministry of Munitions. It is published with the consent of the General Staff of the War Office.

Ethoxydichloroarsine.

When molecular quantities of sodium ethoxide and arsenic trichloride were employed, the action could be regulated so as to proceed according to the equation

$$NaOEt + AsCl_3 = NaCl + EtO{\cdot}AsCl_2.$$

A solution of 15 grams of sodium (1 atom) in 300 c.c. of ethyl alcohol was gradually added, within an interval of two and a-half hours, to 118 grams of commercial arsenic trichloride (1 mol.). The mixture was kept cool by immersion in cold water, and was shaken after each addition of the ethoxide. The product was then heated for one hour longer, the sodium chloride separated, and the excess of alcohol removed.

Ethoxydichloroarsine, $EtO{\cdot}AsCl_2$, is a colourless liquid which boils at 145—146°/751 mm., whereas arsenic trichloride, according

to Thorpe, boils at 130·2°/760 mm. The yield amounted to 70 grams, which is 59 per cent. of the theoretical.

Found: As = 39·04. Cl = 37·2.

$C_2H_5OCl_2As$ requires As = 39·27; Cl = 37·1 per cent.

Ethoxydichloroarsine fumes on exposure to air. When poured into cold water, a copious precipitate of arsenious oxide is immediately formed.

Diethoxychloroarsine.

It is also possible to regulate the action of sodium ethoxide on arsenic trichloride, so that two ethoxy-groups are introduced into the molecule of the latter.

A solution of 30 grams of sodium (2 atoms) in 600 c.c. of ethyl alcohol was added slowly to 118 grams of arsenic trichloride (1 mol.). The addition of the ethoxide lasted two and a-half hours. After twenty-four hours at the ordinary temperature, the mixture was heated for one hour, the sodium chloride separated, and the excess of alcohol removed. The residual liquid was distilled under diminished pressure.

Diethoxychloroarsine, $(OEt)_2AsCl$, is a colourless liquid, which boils at 64—65°/20 mm. and at 159—160°/760 mm.

The yield was 90 grams, which is 69 per cent. of the theoretical.

Found: As = 37·6. Cl = 17·3.

$C_4H_{10}O_2ClAs$ requires As = 37·4; Cl = 17·7 per cent.

The behaviour towards water is similar to that of ethoxydichloroarsine.

Ethyldichloroarsine.

Ethyldichloroarsine was obtained by La Coste (*Annalen*, 1881, **208**, 33) by the action of arsenic trichloride on mercury diethyl:

$$AsCl_3 + HgEt_2 = AsEtCl_2 + HgEtCl.$$

This method was obviously unsuitable for the preparation in quantity of this compound. The following method gave a satisfactory result.

Auger (*Compt. rend.*, 1903, **137**, 925) having shown that sulphur dioxide reduces sodium methylarsinate to methylarsenious oxide, the reduction of magnesium ethylarsinate (Dehn, *Amer. Chem. J.*, 1905, **33**, 132) was conducted in the following manner. Thirty-four grams of the salt were added to 250 c.c. of water, 10 grams of iodine added, and a current of sulphur dioxide was passed into the solution for four and a-half hours. The clear solution gradually became turbid, owing to the separation of a canary-

yellow precipitate. This would indicate that the ethylarsinic acid had been reduced to ethylarsenious oxide, EtAsO, which, with hydrogen iodide, formed ethyldi-iodoarsine, $EtAsI_2$.

We found, however, that the preparation of the magnesium salt was unnecessary as a preliminary stage for the isolation of ethyldi-iodoarsine, as the latter compound could be prepared directly in the following manner.

Arsenious oxide (159 grams) was dissolved in a solution of sodium hydroxide (193 grams) in 500 c.c. of water. The solution was poured into 1400 c.c. of water, ethyl iodide (250 grams) added, and then sufficient rectified spirit to form one phase. The mixture remained at the temperature of the laboratory for six days. After removal of the bulk of the alcohol, the residual liquid (1300 c.c.) was acidified with concentrated hydrochloric acid, the precipitate removed, and a current of sulphur dioxide passed into the filtrate. The colour of the iodine quickly disappeared, and the yellow ethyl di-iodoarsine began to separate as an oil. The sulphur dioxide was passed for about three and a-half hours, 330 c.c. of concentrated hydrochloric acid being added at intervals. The oil was separated from the liquid. In this case there was no solid present, but in other preparations, where the original concentration of the mixture resulting from Meyer's reaction had been carried further than in the present case, a mixture of solid and oil resulted. It is convenient to adjust the concentration so that only oil separates. From the yellow, aqueous liquid a small additional amount of oil was obtained by the further addition of hydrochloric acid and sulphur dioxide. The yield of ethyldi-iodoarsine was 272 grams.

For the conversion of this quantity of ethyldi-iodoarsine into ethylarsenious oxide, the oil was dissolved in 750 c.c. of benzene and a mixture of 60 grams of calcium chloride and 192 grams of anhydrous sodium carbonate added. After the mixture had been heated on the water-bath for two hours, the yellow colour disappeared. The solution was poured off, and the residual solid extracted with benzene. The benzene was distilled from the solution, and the resulting oil heated until its temperature was about 120°. The yield of ethylarsenious oxide was 100 grams.

For the conversion of the oxide into ethyldichloroarsine according to the equation

$$EtAsO + 2HCl = EtAsCl_2 + H_2O,$$

100 grams were placed in a separating funnel, and 25 c.c. of concentrated hydrochloric acid were added. The funnel was then surrounded with cold water, and a current of hydrogen chloride passed through the oil for about three hours, the completion of the reaction being shown by the escape of hydrogen chloride by

exit tube. The oil was separated, dried with calcium chloride, ed as far as possible from hydrogen chloride by means of a rent of carbon dioxide, and distilled. Twenty-nine grams of a ction of lower boiling point, containing a considerable propor- n of ethyldichloroarsine, were first collected. The product boil- ; between 150° and 155° amounted to 101 grams. The com- und can be obtained quite pure by fractionating further.

In connexion with the preparation of ethyldichloroarsine in antity, the following points which emerge from the preceding scription are worthy of notice: (1) Sodium hydroxide may be ed in place of the more expensive potassium hydroxide in Meyer's action. (2) The separation of magnesium ethylarsinate is un- cessary. (3) The sodium iodide formed in the first reaction is ilised, and no further addition of the expensive potassium iodide required, as is the case if the magnesium salt is first isolated and ien reduced. (4) There is a considerable saving of time.

The following are the details of the yields in several of the reparations:

Ethyl iodide. Grams.	Ethylarsenious oxide. Grams.	Ethyldichloroarsine. Grams.
250	100	101
	85	87
	92	89
	93	99
	95	97
	100	107
	99	
	111	
	109	
	93	
500	178	

The yield of ethyldichloroarsine is really better than is represented above, since a fair quantity can be recovered from the distillates of lower boiling point on fractionation. The yield of ethylarsenious oxide is more than 50 per cent., calculating on the ethyl iodide initially used; the yield calculated from the ethyl iodide actually entering into reaction is very much greater, since a considerable quantity of ethyl iodide can be recovered. The yield of ethyldichloroarsine from ethylarsenious oxide is more than 80 per cent. of the theoretical.

It was thus clear that the yield would probably be improved by elevating the temperature at which the first stage (Meyer's reaction) took place. Experiments were begun to substitute ethyl chloride for the more expensive ethyl iodide, but the work was stopped at this point, when the conclusion was reached that it

would be necessary to carry out the reaction with ethyl chloride under pressure.

Phenylethoxychloroarsine.

This compound was prepared according to the equation

$$PhAsCl_2 + NaOEt = NaCl + PhAsCl{\cdot}OEt.$$

4·6 Grams of sodium (1 atom) were dissolved in 100 c.c. of ethyl alcohol, and the solution was gradually added to 44·6 grams of phenyldichloroarsine (1 mol.) during half an hour. The mixture was then heated on the water-bath for two and a-half hours, cooled, the sodium chloride and then the alcohol removed, and the residue distilled under diminished pressure.

Phenylethoxychloroarsine, PhAsCl·OEt, is a colourless oil which boils at 125—126°/12 mm. The yield was 37 grams, or 80 per cent. of the theoretical.

Found: Cl = 15·1.

$C_8H_{10}OClAs$ requires Cl = 15·2 per cent.

It gradually undergoes hydrolysis when kept in contact with water, being transformed into a white solid, which, when crystallised from petroleum (b. p. 90—105°), separates in needles melting at 127—130°. It is curious that this product has a melting point considerably higher than that recorded in the literature for phenylarsenious oxide.

Formation of Unstable Cyano-compounds.

Evidence was obtained that the following compounds are very unstable, owing to the ease with which they underwent hydrolysis: phenylchlorocyanoarsine, phenyldicyanoarsine, and ethyldicyanoarsine. It was not found possible to isolate them.

Action of Hydrogen Cyanide on Diphenylethoxyarsine: Diphenylcyanoarsine.

Diphenylchloroarsine was treated with sodium ethoxide,

$$Ph_2AsCl + NaOEt = Ph_2As{\cdot}OEt + NaCl,$$

the resulting ethoxy-compound being then acted on by hydrogen cyanide,

$$Ph_2As{\cdot}OEt + HCN = Ph_2As{\cdot}CN + EtOH.$$

2·3 Grams of sodium (1 atom) were dissolved in 100 c.c. of ethyl alcohol, and the solution was added to 26 grams of pure diphenylchloroarsine (1 mol.) dissolved in 50 c.c. of ethyl alcohol. The addition lasted one hour. After the mixture had been heated for one hour on the water-bath, the sodium chloride and the alcohol

were removed. The residue was a viscid oil, which solidified partly when kept overnight. It was then heated at 140° for three hours in a current of dry hydrogen cyanide. On cooling, the oil was washed with water, and a nucleus of the solid form of diphenylcyanoarsine, prepared by the method described later, was added; this caused the oil to crystallise. The product was washed with light petroleum and dried under diminished pressure. Twenty grams of a solid melting at 30—34° were obtained, and this corresponds with an 80 per cent. yield of diphenylcyanoarsine.

Action of Hydrogen Cyanide on Diphenylarsenious Oxide.

Diphenylcyanoarsine was next prepared by converting diphenylchloroarsine into diphenylarsenious oxide, which was then acted on by hydrogen cyanide:

$$2Ph_2AsCl + 2NaOH = H_2O + 2NaCl + Ph_2As{\cdot}O{\cdot}AsPh_2,$$
$$Ph_2As{\cdot}O{\cdot}AsPh_2 + 2HCN = 2Ph_2As{\cdot}CN + H_2O.$$

The product obtained by the action of gaseous hydrogen cyanide on molten diphenylarsenious oxide was distilled under diminished pressure.

Diphenylcyanoarsine boils at 213°/21 mm. (Found: N = 5·4. $C_{13}H_{10}NAs$ requires N = 5·5 per cent.).

From 25 grams of diphenylarsenious oxide, yields of 23 and 24 grams, respectively, of the pure, redistilled oil were obtained in successive experiments, corresponding with a yield of about 90 per cent. of the theoretical.

A most important property of this compound is the fact that it is sensitive to alkali in a remarkable degree. This was first noticed when a thin film of the oil, prepared as just described, was left exposed to the atmosphere in a crystallising dish at the ordinary temperature. The film was gradually converted into a solid, and it appeared that the oily diphenylcyanoarsine had crystallised. On examining the solid, it was found, however, that it consisted of diphenylarsenious oxide, as a determination of the melting point both alone and in presence of some of the oxide showed. It was proved that the result was not due to the presence of unattacked diphenylarsenious oxide in the original oil, and the inference was that the conversion of the oily cyano-compound into the oxide had been effected catalytically by the alkali of the glass vessel. It was next found that the oil solidified fairly quickly when kept in contact with *N*/10-aqueous sodium hydroxide at the ordinary temperature, and very quickly when warmed with alkali of this strength. A portion of the solid obtained in this manner was crystallised

from light petroleum, and a determination of its melting point showed that it consisted of diphenylarsenious oxide.

This interesting change may occur in the following stages:

$$Ph_2As{\cdot}CN + H_2O = Ph_2As(CN)<^{H}_{OH},$$

$$Ph_2As(CN)<^{H}_{OH} = Ph_2As{\cdot}OH + HCN,$$

$$2Ph_2As{\cdot}OH = H_2O + Ph_2As{\cdot}O{\cdot}AsPh_2.$$

The solid modification of diphenylcyanoarsine was obtained in the following manner. The crude oil resulting from the action of hydrogen cyanide on diphenylarsenious oxide was washed twice with water, and left in contact with solid calcium chloride overnight. It was then found to consist of a solid and very little oil. A portion of the solid was then washed with light petroleum, and found to melt at about 31—32° (Sturniolo and Bellinzoni, *Gazzetta*, 1919, **49**, ii, 326, give 35°). A nucleus added to some of the pure oil caused the latter to crystallise immediately.

According to La Coste and Michaelis (*Annalen*, 1880, **201**, 222), diphenylchloroarsine is only sparingly soluble in sodium hydroxide or potassium hydroxide on heating. The mobility of the halogen in diphenylchloroarsine is, however, much greater than would be inferred from the data in the literature; the chlorine can be displaced very easily under the following conditions, and the method now described is a convenient one for the preparation of diphenylarsenious oxide in quantity.

Sodium hydroxide (325 grams) was dissolved in water (1500 c.c.), and, when the temperature of the solution had fallen to 50°, diphenylchloroarsine (500 grams) was added. The solid melted, and the temperature was then gradually raised to 70° within fifteen minutes, during which time the mixture was stirred vigorously. When once the oil began to harden, it was transformed in the course of a few minutes into a hard solid. The temperature was maintained at 70° for fifteen minutes longer, with occasional stirring, and, when cold, the liquid was decanted from the solid, which was then powdered and thoroughly washed with water until the washings were free both from alkali and chloride. The oxide was then collected and dried on porous plates. If kept at the ordinary temperature, the product at this stage becomes constant in weight very slowly. It was found practical to dry in air for a day at the ordinary temperature, and then at 60° to 70° until the weight was constant. The yield of anhydrous oxide was 435 grams, which is 97 per cent. of the theoretical. When crystallised from light petroleum, the oxide melts at 92·5—93·5°, whereas La Coste and Michaelis (*loc. cit.*) give 91—92°.

› action took place in accordance with the equation

$$2Ph_2AsCl + 2NaOH = 2NaCl + H_2O + Ph_2As{\cdot}O{\cdot}AsPh_2.$$

the majority of our experiments on the preparation of ›nylcyanoarsine, 150 grams of diphenylarsenious oxide were each time. The flask containing this was placed in a bath of ·le metal, the temperature of which was gradually raised from to 160°. Dry hydrogen cyanide was passed for about five s through the molten diphenylarsenious oxide. The contents ne flask were allowed to cool, and, while still slightly warm, › poured into a porcelain dish, when solidification took place lually. The yield of uncrystallised product was practically ›retical. If it is desired to keep the product for any length of ›, it should be dried under diminished pressure until constant veight.

t was also found that diphenylcyanoarsine can be obtained by ›wing diphenylarsenious oxide to remain in contact with a con- trated aqueous solution of hydrogen cyanide at the ordinary ıperature. The action of anhydrous hydrogen cyanide on ›henylarsenious oxide at the ordinary temperature would, in our .nion, be the most convenient method of preparing this com- und on the large scale, especially if it is desired to obtain a oduct which will be fairly stable on keeping.

Our first experiment on the preparation of diphenylcyanoarsine ıs made with diphenylchloroarsine and potassium cyanide, but, the ease with which the compound was hydrolysed was recog- .sed at an early stage, the use of an aqueous solution of potassium ranide was purposely avoided, as we were convinced that the ıethod would be unsuitable for the preparation of the compound ı a state of purity. The following experiment, carried out at a ıter stage with rectified spirit as the solvent, may, however, be uoted in this connexion. A mixture of 133 grams of diphenyl- hloroarsine and 50 grams of potassium cyanide was gently heated ınder reflux for five hours with 250 c.c. of rectified spirit. The iquid gradually darkened, and ultimately became red. It was .eft overnight, and the solid was removed. The filtrate separated into two layers. To the lower layer (47 grams), a nucleus of the solid diphenylcyanoarsine was added, and crystallisation began slowly. After one day in the ice-chest, the crystalline deposit amounted to 18 grams; when washed with ether, it melted at 32—34°. The upper layer was mixed with an excess of water. The resulting oil (61 grams) was removed, the aqueous solution being extracted with ether, and the ethereal solution added to the oil. To this ethereal solution were also added the ethereal wash- ings from the 18 grams. The ethereal solution was dried with

sodium sulphate, the ether distilled, the residue mixed with th liquid portion of the original lower layer, and the whole heate at 140—150° to remove all the ether and alcohol. After a fort night in the ice-chest, 50 grams of solid and 47 grams of liqui were present. The total yield of solid cyano-compound was 6 grams, and of solid plus liquid 115 grams.

It is certain that, when aqueous potassium cyanide is used, some of the diphenylchloroarsine will be converted into diphenylarsenious oxide, owing to the alkalinity of the liquid, and it is equally certain that, unless special precautions are taken, the diphenylcyanoarsine formed will, on keeping, undergo change owing to catalytic hydrolysis.

It is desirable that the hydrolysis of diphenylcyanoarsine should be examined more fully than has been described in the present paper, in order that conditions may be arrived at whereby the substance does not undergo alteration on keeping.

Action of Chlorine on Diphenylcyanoarsine.

The action represented by the equation

$$Ph_2As{\cdot}CN + Cl_2 = Ph_2As(CN)Cl_2,$$

was investigated.

Twenty grams of diphenylcyanoarsine were dissolved in 100 c.c. of benzene, and a current of chlorine was passed through the cooled solution. Solid began to separate, and the passage of the chlorine was continued until the liquid was green in tint. On removal, the solid fumed in air; it melted indefinitely at about 115°, and contained chlorine but no nitrogen. On boiling with water, it dissolved, and, on cooling, needles of diphenylarsinic acid separated. It seems likely that the compound in question was diphenylarsenic oxychloride, $(Ph_2AsCl_2)_2O$, which melts at 117° (La Coste and Michaelis, *Annalen*, 1880, **201**, 230), produced by the hydrolysis of the cyano-group, thus:

$$Ph_2AsCl_2{\cdot}CN + H_2O = Ph_2AsCl_2{\cdot}OH + HCN,$$
$$2Ph_2AsCl_2{\cdot}OH = H_2O + Ph_2AsCl_2{\cdot}O{\cdot}Ph_2AsCl_2,$$

whilst its conversion into diphenylarsinic acid would be interpreted as follows:

$$Ph_2AsCl_2{\cdot}O{\cdot}Ph_2AsCl_2 + 4H_2O = 4HCl + Ph_2As(OH)_2{\cdot}O{\cdot}Ph_2As(OH)_2,$$
$$Ph_2As(OH)_2{\cdot}O{\cdot}Ph_2As(OH)_2 + 2HCl = H_2O + 2Ph_2AsCl(OH)_2,$$
$$Ph_2AsCl(OH)_2 + H_2O = HCl + Ph_2As(OH)_3,$$
$$Ph_2As(OH)_3 = H_2O + Ph_2AsO{\cdot}OH.$$

When the addition of chlorine to diphenylcyanoarsine was con-

ted with dry benzene or dry carbon tetrachloride as the solvent, milar result was obtained.

In allowing the benzene filtrate in the first experiment to remain several days at the ordinary temperature, a crystalline product gradually deposited, which softened at 123° and melted at °. It amounted to 2 grams, and contained both nitrogen and orine. Another quantity of this substance was obtained from imilar experiment, the difference between it and the first sample ng in the somewhat higher melting point, namely, 130—133°. e product, in fact, appeared to be *diphenylcyanoarsine dichloride*, $_2As(CN)Cl_2$.

Found: Cl = 22·0.

$C_{13}H_{10}NCl_2As$ requires Cl = 21·8 per cent.

When once it had been isolated, it was apparently fairly stable hen dry, since it underwent no change when kept in a desiccator r three weeks. When boiled with water, it dissolved completely, nd needles of diphenylarsinic acid separated on cooling, as represented by the equations

$$Ph_2As(CN)Cl_2 + 3H_2O = HCN + 2HCl + Ph_2As(OH)_3,$$
$$Ph_2As(OH)_3 = H_2O + Ph_2AsO{\cdot}OH.$$

Action of Sodium Hydrosulphide on Diphenylchloroarsine.

This action was studied in order to ascertain if diphenylarsine hydrosulphide could be formed, thus:

$$Ph_2AsCl + NaSH = Ph_2As{\cdot}SH + NaCl.$$

The product consisted, however, of diphenylarsenious sulphide, which was presumably formed by the elimination of hydrogen sulphide from the hydrosulphide:

$$2Ph_2As{\cdot}SH = H_2S + Ph_2As{\cdot}S{\cdot}AsPh_2.$$

The yield was 83 per cent. of the theoretical.

The authors desire to acknowledge the valuable assistance rendered by Miss Agnes Paterson Millar, B.Sc. (Mrs. Cleland), Miss Nellie Walker, M.A., B.Sc., and the late Mr. George Fyfe Elder.

UNIVERSITY COLLEGE, DUNDEE,
UNIVERSITY OF ST. ANDREWS. [*Received, March 11th, 1920.*]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 25TH, 1920, AT 5 P.M.

Sir JAMES J. DOBBIE, M.A., D.Sc., F.R.S., President, in the Chair.

Dr. H. BASSETT and Mr. A. STEVENSON were elected Scrutators, and the ballot for the election of Officers and Council was opened.

The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending December 31st, 1919, was proposed by Dr. F. L. PYMAN, seconded by Mr. E. GRANT HOOPER, and carried.

REPORT OF COUNCIL, 1919—1920.

A substantial addition to the number of Fellows was reported for 1918, and the Council is gratified to record a still greater increase during the past year. On December 31st, 1918, the number of Fellows was 3,401. During 1919, 274 were elected and 18 reinstated, making a gross total of 3,693. The Society has lost 43 Fellows by death, 42 resignations have been received, the election of 1 has been declared void, and the names of 38 have been removed for non-payment of Annual Subscription. The total number of Fellows, therefore, on December 31st, 1919, was 3,569, showing a net increase of 168, as against 131 the previous year.

It is with deep regret the Council has to report that the following Fellows have died:

Herbert Anderson (1895).	William James Cousins (1885).
William Beam (1903).	Sir William Crookes (1857).
David Bendix (1874).	Walter Henry Dixon (1912).
Richard Blenkinsop (1902).	William Lofland Dudley (1890).
Arthur Anderson Bones (1912).	Owen Charles Edwards (1918).
John Richard Brooke (1900).	Arthur Henry Elliott (1878).
Adrian John Brown (1876).	Philip Anderson Estcourt (1888).
Herbert Stoddard Coleman (1913).	Thomas Fairley (1865).

George Carey Foster (1856).
William Humphrey Gibson (1888).
Harold Cecil Greenwood (1916).
Samuel Godfrey Hall (1899).
Augustus George Vernon Harcourt (1859).
John Holmes (1897).
Henry Owen Huskisson (1861).
George Frederic Kendall (1884).
John Falconer King (1876).
Edward Gurley Love (1882).
Thomas Morison Maben (1915).
James Baird MacLachlan (1916).
George Martineau (1871).
Arthur Sampson Napier (1874).
William Henry Oates (1893).
Walter Parker (1917).
Francis Reginald Power (1884).
Sir Boverton Redwood (1866).
Norman Scott Rudolf (1909).
Alfred Ulrich Max Schlaepfer (1918).
John Emilius Lancelot Shadwell (1880).
Harry Shulman (1915).
Sir Peter Wyatt Squire (1882).
James Fleming Stark (1870).
John Charles Umney (1893).
Elwyn Waller (1878).
Christopher Joseph Whittaker (1899).

The Council has to mourn the loss of three Past-Presidents, Sir William Crookes, O.M., Dr. A. G. Vernon Harcourt, and Prof. J. Emerson Reynolds. Obituary notices of these and other Fellows will appear in the Transactions in due course.

Resignations have been received from:

Paul Seidelin Arup (1906).
Thomas James Bandinel (1916).
Frank Bayley (1917).
William Charles Trevor Beasley (1917).
John Cardew Bedwell (1901).
William Berry (1888).
Wilfred William O. Beveridge (1903).
Robert Bickerstaffe (1908).
William George Brown (1884).
Alexander Caruth (1913).
Pinzen Cheng (1915).
Joseph Morgan Davey (1905).
John Arthur Dewhirst (1899).
Edward Percy Frankland (1912).
George Pomeroy Furneaux (1909).
Henry Wippell Gadd (1901).
George Harrison Gemmell (1885).
Stanton Gibson (1913).
Arthur Frank Girvan (1908).
Alfred Rowland Gower (1893).
Herbert Green (1878).
Edgar Percy Hedley (1906).
Arthur Edward Holme (1895).
Robert John Hughes (1918).
Edgar Jobling (1912).
James Johnstone (1896).
Charles John J. Mansford (1897).
Frank Clifford Marchant (1913).
Robert Mills (1911).
John Charles Henderson Mingaye (1887).
Louis Murgatroyd (1907).
Frank Henry Pugh (1917).
Louis John Ezekiel Riley (1904).
Conrad Howard Rogers (1916).
John George Rose (1910).
William Charles Ross (1902).
Ernest William Smith (1910).
James Thomas Stevenson (1909).
Alan West Stewart (1914).
Cedric Gerard Verver (1917).
Alexander Watt (1877).
William Henry Withey (1908).

The congratulations of the Society are offered to Mr. Thomas Fogg, who, having been elected on November 17th, 1859, has completed sixty years as a Fellow, and to the following, who have attained their jubilee as Fellows:

	Elected.
William Henry Deering	April 1st, 1869.
James Thomson Bottomley	April 15th, 1869.
William James Lewis	Nov. 4th, 1869.
George Robertson Hislop	Jan. 20th, 1870.
David Brown	Mar. 17th, 1870.
Alexander Muirhead	Mar. 17th, 1870.

Since the last Annual General Meeting, the Society has lost two Honorary and Foreign Members, Prof. A. P. N. Franchimont and Prof. Alfred Werner. Sir Edward Thorpe and Prof. G. T. Morgan, respectively, have undertaken to prepare obituary notices of these distinguished chemists.

The volume of Transactions for 1919 contains 1,517 pages, of which 1,392 pages are occupied by 139 memoirs, the remaining 125 pages being devoted to Obituary Notices, lectures on special subjects, the Report of the Annual General Meeting, the Presidential Address, and the Report of the International Committee on Atomic Weights. The volume for the preceding year contained 89 memoirs, occupying 849 pages. The Journal for 1919 contains also 2,534 abstracts, occupying 1,148 pages, whilst the abstracts for 1918 numbered 2,436 and occupied 1,032 pages. In the last Report, in referring to the great and continuous decrease since the start of the war in the number of memoirs published in journals devoted to chemistry and allied subjects, the view was expressed that the lowest point had probably been reached and that an increase in the number of papers abstracted might be anticipated. This view has been justified; the number has shown a decided increase, especially in the latter part of the year, and a very considerable increase seems to be indicated for 1920.

The abstracts may be classified as follows:

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	—	823
Physiological Chemistry	—	144
Chemistry of Vegetable Physiology and Agriculture	—	186
	616	1,153
PART II.		
General and Physical Chemistry	—	636
Inorganic Chemistry	—	239
Mineralogical Chemistry	—	57
Analytical Chemistry	—	449
	532	1,381
Total in Parts I. and II.	1,148	2,534

ɔonnexion with the revision of the Bye-laws, to which refer-
ʀas made in the last Report of Council, an Extraordinary al Meeting of the Society was held on May 8th, 1919. At neeting, eight resolutions dealing with various modifications e constitution of the Society were passed (see Proc., 1919,), and the Council was authorised to secure a supplemental ter giving the power to make the necessary alterations in the aws. The petition praying for such supplemental Charter presented to the Privy Council last July, and His Majesty has been graciously pleased to grant the request of the Society. supplemental Charter has been received, and an Extraordinary eral Meeting will be summoned at an early date to consider the rations in the Bye-laws proposed by the Council under the new litions.

eference was made in last year's Report to the question of publication of Chemical Compendia in the English language. scheme set forth in the Report of the General Committee of Chemical and Allied Societies was at a later date duly approved the Council, and its further development was placed in the ıds of the Federal Council for Pure and Applied Chemistry. e decision of the Council was communicated to the French and aerican Chemical Societies, to those societies represented on the neral Committee, and to the Department of Scientific and Indus-al Research, which later intimated that it would be prepared consider an application from the Federal Council for financial sistance.

The question of the supply of chemical glassware and fine iemicals for research purposes, raised by the Department of cientific and Industrial Research, has received the earnest atten-on of the Council. Its considered opinion on these matters as communicated to the Department of Scientific and Industrial Research, and the views of the Council were expressed in greater letail by a deputation which waited on the Department.

The Council have accepted from the Harrison Memorial Committee the administration of a Trust Fund for Research purposes and of a Memorial to the late Lieut.-Colonel E. F. Harrison, C.M.G., Director of the Chemical Warfare Department of the Ministry of Munitions. A position for the memorial has been found on the upper part of the arch outside the Meeting Room, and it is intended that the names of all those Fellows who fell in action or died on service shall appear in close proximity to the memorial.

A collection of letters and portraits received by the late Sir Henry E. Roscoe from eminent scientific men of his time has been pre-

sented to the Society by Miss Roscoe, to whom the Council has expressed its appreciative thanks for this interesting and valuable gift.

The first of the three Lectures arranged by the Council to be delivered during the present Session was given on December 18th by Prof. James Walker, who chose as his subject "War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes." The lecture on "Some War-time Efforts in Chemical Industry at Gretna," which was to have been delivered on March 4th by Mr. John C. Burnham, has been unavoidably postponed. The third of the series will be given on June 17th by Prof. J. C. McLennan, who will lecture on "Helium." The Council is gratified to find that the delivery of lectures on special subjects continues to meet with appreciation from the Fellows, and regrets that the seating accommodation afforded by the Meeting Room is inadequate for these occasions.

Prof. A. W. Crossley and Dr. A. Scott have consented to act as the Society's representatives on the Conjoint Board of Scientific Societies, whilst Prof. H. E. Armstrong, Sir William J. Pope, and Sir William A. Tilden have been reappointed as the Society's representatives for the current year on the Federal Council for Pure and Applied Chemistry. The Council has further nominated Dr. J. C. Cain, Mr. A. J. Greenaway, Mr. C. A. Hill, Prof. J. M. Thomson, and Prof. F. Soddy to serve on the Sub-Committees of the Imperial Mineral Resources Bureau.

The Celebrations held by the French Chemical Society in Paris on June 5th and 6th, 1919, were attended by Sir William J. Pope as the Society's representative.

Permission was given to Dr. Kling, Director of the Laboratoire Municipale de Paris, to issue a French translation of the Annual Reports for 1918, and this was published in the early part of 1920 by Messrs. Gauthier-Villars et Cie.

At the request of the American Chemical Society, the Council has appointed a Committee, consisting of the Officers and the Editors, to co-operate with corresponding Committees appointed by the American Chemical Society and the Society of Chemical Industry to consider questions of Nomenclature, Spelling, and Pronunciation.

At the suggestion of Prof. P. A. Guye, the Council has agreed to refer the question of publishing Tables of Physico-Chemical Symbols to the Union Internationale de la Chimie Pure et Appliquée.

The Council desires to record its thanks to those Fellows who have contributed to Vol. XVI. of the Annual Reports, and to the Abstractors for their services during the past year.

circular was issued to Fellows on January 23rd, 1920, stating ;, subject to sufficient support being received, it was proposed nold a Soirée at the Natural History Museum on the evening Thursday, March 25th, the day of the Annual General Meeting. ing, however, to insufficient support being forthcoming, the incil was reluctantly compelled to abandon the proposal.

The scheme for the extended use of the Library has now been full operation since May 1st, 1919, and the fact that during the ditional hours of opening the Library, 1,198 attendances were corded, affords evidence that these extra facilities are appreciated. s already announced, the Library is now open until 9 p.m. every eek-day except Saturday, when it closes at 5 o'clock.

The expenditure incurred during 1919 in enlarging the scope of ie Library amounted to £439, of which sum £406 10*s*. as received from the following Societies: Association of British hemical Manufacturers, Biochemical Society, Faraday Society, nstitute of Chemistry, Society of Chemical Industry, Society of Dyers and Colourists, and the Society of Public Analysts. It is stimated that from £550 to £600 will be required to continue the cheme during 1920.

The number of books borrowed from the Library during 1919 vas 2,867, as against 2,905 in 1918. The additions to the Library comprise 189 books, 338 volumes of periodicals, and 86 pamphlets, as compared with 126, 255, and 31, respectively, the previous year.

The accounts for the year 1919 show a balance of income over expenditure amounting to £522 3*s*. 3*d*., as against £2,489 4*s*. 4*d*. reported last March for the previous year, and it is now necessary to recognise that the prevailing high costs are rapidly overtaking the economies due to diminished printing during the War. Thus, although the income from all sources amounts to £11,838 1*s*. 7*d*., and exceeds that recorded for 1918 by £1,755 6*s*. 8*d*., the expenditure has increased by £3.722 7*s*. 9*d*., reaching the sum of £11,315 18*s*. 4*d*.

On examining the details of income and expenditure, it will be found that the increase of revenue arises from additional life compositions £263, admission fees £148, and subscriptions £315, together with £138 15*s*. 5*d*. from interest on increased investments, £417 12*s*. 4*d*. from sale of publications, and £574 14*s*. 11*d*. representing increased gross proceeds from advertisements in the JOURNAL.

The very serious increase of £3,722 7*s*. 9*d*. in expenditure is owing principally to the cost of the Society's publications, which aggregates £8,034 13*s*. 5*d*., as against £5,247 11*s*. 9*d*. for 1918, an excess of £2,787 1*s*. 8*d*. This is in some measure due to the

expected partial recovery in the volume of Transactions, as indicated by the following synopsis:

	Number of Pages.		
	Trans.	Abstr.	Total.
1914	2,909	2,068	4,977
1915	1,862	1,944	3,806
1916	1,368	1,532	2,900
1917	1,128	1,308	2,436
1918	995	1,032	2,027
1919	1,517	1,148	2 665

In so far as this represents an increased production of original work, it is a gratifying feature of the Peace year, but the enhanced cost of printing the JOURNAL, which rose from £2,750 8*s*. 3*d*. in 1918 to £4,625 2*s*. 7*d*. in the year under review, is the cause of grave anxiety to the Council. At its request, the situation has been explored by the Finance Committee, but it has not been found possible to devise any practicable remedy; it appears from the inquiry that the position of the Society is less unfavourable than that of some other similar bodies. Nevertheless, the fact that the cost of the JOURNAL per page has now reached £2 4*s*. 8*d*., in comparison with 17*s*. 9*d*. in 1914, will shortly become the source of deep embarrassment, because a return to pre-war volume unaccompanied by a diminution in cost of production would confront the Society with an expenditure of £12,000 on the JOURNAL alone, involving a deficit approximating to £4,000 per annum.

Having regard to this forecast, the Council considers it a duty to urge upon authors the most rigid observance of word-economy in expressing their ideas and the restriction of experimental details within the smallest possible compass.

The necessity of increasing the remuneration made to the staff has been the principal cause of a rise in administrative expenses from £1,681 6*s*. 5*d*. in 1918 to £2,220 7*s*. 4*d*. in 1919.

£2,000 National War Bonds were purchased early in the year, and £480 invested in Funding Loan, but the estimated value of the Society's investments on December 31st, 1919, was only £1,291 10*s*. 10*d*. higher than at the corresponding date a year before.

The following grants have been made from the Research Fund during the year:

The physical chemical properties of beryllium compounds. A. J. Allmand..	£10	0	0
The formation of binary and ternary mixtures of constant minimum boiling point in a group of organic liquids. W. R. G. Atkins..	10	0	0

	£	s.	d.
Formation and stability of spiro-compounds. O. Becker ...	£15	0	0
(*a*) Physiologically active bases. (*b*) Spirane bases with a view to resolution into optically active components. G. M. Bennett	5	0	0
Oximino-derivatives. O. L. Brady..................................	10	0	0
The biochemistry of iodine. A. T. Cameron.....................	15	0	0
Action of sulphuretted hydrogen on organic compounds containing unsaturated linkages. F. Challenger	10	0	0
The constitution of carbazole blue. M. Copisarow	20	0	0
Study of the addition of alkyl haloids to ethyl β-diethylaminocrotonate. P. W. Denny	10	0	0
Derivatives of xanthene. S. N. Dhar	10	0	0
Isomerism of the oximes. F. P. Dunn	10	0	0
Ring formation of organic compounds. E. H. Farmer	15	0	0
The constitution of weak acids and their salts. J. C. Ghosh	30	0	0
(*a*) Preparation of substituted glutaric acids. (*b*) Constitution of Guareschi's spiro-compounds. W. H. Gough	15	0	0
Action of halogens upon dichlorodimethyl*cyclo*hexadiene. L. E. Hinkel..	15	0	0
Condensation of ethyl sodiomalonate with glycolchlorhydrin. J. Kenner...	10	0	0
The solubility relationships of 4-dimethylamino-1-phenyl-3-methylpyrazole. H. King....................................	5	0	0
Formation of ketones from acids of the glutaric series and the formation of bridged-ring compounds. G. A. R. Kon...	15	0	0
The properties of certain binary mixtures of liquids. J. I. O. Masson	10	0	0
A quantitative method of determining the velocity of coagulation. J. N. Mukherjee	15	0	0
The reactivity of sulphur chloride with amino- and amido-compounds. K. G. Naik	10	0	0
Attempted synthesis of myricetin. M. Nierenstein	10	0	0
Action of diazomethane on α-diketones and on acyl chlorides. M. Nierenstein..	15	0	0
The investigation of gallotannin (contd.). M. Nierenstein...	15	0	0
The relationship between melting point, chemical composition and physical properties of series of organic compounds. P. W. Robertson	8	0	0
The latent heat of fusion of palmitic acid and other fatty acids. (Mrs.) K. Stratton..	20	0	0
The conversion of borneol into camphene and the study of analogous reactions. (Miss) M. Tadman	10	0	0
Influence of the constitution of tertiary bases on the rate of formation of quaternary ammonium salts (contd.). E. R. Thomas	15	0	0
Total	£358	0	0

Whilst the aggregate grants exceeded by £261 14*s*. 0*d*. the corresponding payments for 1918, the balance of income over expenditure for 1919 is £349 13*s*. 11*d*., as against £539 13*s*. 9*d*. for the

previous year. The return on investments was £24 6*s*. 5*d*. higher, and £91 0*s*. 10*d*. was realised by sale of gold and platinum; on the other hand, the repayment of grants was £44 14*s*. 6*d*. less than during 1918, and the recovery of income-tax was £13 5*s*. 4*d*. lower. £300 National War Bonds were purchased for this account in 1919.

A vote of thanks to the Auditors, proposed by the TREASURER and seconded by Mr. F. G. POPE, was carried unanimously, Dr. C. K. TINKLER making acknowledgment.

Professor H. BRERETON BAKER proposed a vote of thanks to the Treasurer, Secretaries, and Council for their services during the past year. This was seconded by Dr. T. SLATER PRICE, and acknowledged by Professor S. SMILES, the retiring Secretary.

The PRESIDENT then delivered his Address, entitled, "The War and Key Industries. with special reference to the Fixed Nitrogen Industry."

A vote of thanks to the President for his services in the Chair during the past year and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions, was proposed by Sir WILLIAM A. TILDEN, and seconded by Dr. ALEXANDER SCOTT. The motion was carried with acclamation, and acknowledged hy the PRESIDENT.

The Scrutators presented their report, and the PRESIDENT declared the following to have been elected as Officers and Council for the ensuing year:

President.—Sir James Johnston Dobbie, M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, C.B.E., M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Julius Berend Cohen, Ph.D., B.Sc., F.R.S.; Frederick George Donnan, M.A., Ph.D., F.R.S.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Samuel Smiles, O.B.E., D.Sc., F.R.S.; James Walker, D.Sc., LL.D., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Liabilities.	£ s. d.	£ s. d.
To Subscriptions received in advance	424 0 0	
(Lady Subscriber)	1 10 0	425 10 0
,, ,, ,, ,,		1914 1 5
,, Sundry Creditors		250 4 1
,, Current Account Overdrawn		
,, Research Fund :—		
As per last Balance Sheet	14896 17 1	
Add Excess of Income over Expenditure for the year	349 13 11	15246 11 0
,, Chemical Society : Excess of Assets over Liabilities :—		
As per last Balance Sheet...	27247 11 9	
Add Excess of Income over Expenditure for the year	522 3 3	27769 15 0
		£45606 1 6

Assets.	£ s. d.	£ s. d.
£6730 Metropolitan Consolidated ... Railway 3 per		
£1050 London and North Western	839 12 0	
cent. Debenture Stock ... ... Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1520 14s. 3d.	1316 1 0	
£1400 India 2½ per cent. Stock ... Debenture Stock	2070 2 0	
£2400 Bristol Corporation 2½ per cent. Preference Stock	3572 2 5	
£4341 Midland Railway 2½ per cent. Debenture Stock	1143 1 0	
£1200 Leeds Corporation 3 per cent. Guaranteed Stock, 1923/53	1460 13 6	
£1500 Transvaal 3 per cent. Debenture		
£1200 North British Railway 3 per cent.	1033 11 0	
Stock	704 8 6	
£700 Canada 3½ per cent. Stock. 1930/50		
£2100 5 per cent. War Stock, 1929/47 }	7040 0 2	
£5100 5 per cent. War Bonds }	480 0 0	
£600 4 per cent. Funding Loan, 1960/90		28522 0 1
(Estimated present value of Investments, £20,538 5s. 8d.)		
,, Sundry Debtors		1506 8 0
,, Subscriptions in Arrear estimated to realise		270 0 0
,, Insurance paid in advance		47 10 10
,, Cash in hand		14 11 7
,, Research Fund :—		
Investments (value when acquired):		
£1000 North British Railway 4 per cent. No. 1	1010 0 0	
Preference Stock	4587 18 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock		
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049 15 11	
£1142 10s. New South Wales 3 per cent. Stock ...	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" ...	1002 16 9	
Stock	1010 0 9	
£1365 Midland Railway 2½ per cent. Debenture Stock	708 6 9	
£806 Victoria 3 per cent. Stock	4267 4 10	
£4498 11s. 0d. 5 per cent. War Stock	900 0 0	
£300 5 per cent. War Bonds, 1928...		14934 2 5
(Estimated present value of Research Fund Investments, £11,549 8s. 1d.)		
,, Cash at Bank...		312 8 7
		£45606 1 6

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KERN,
Chartered Accountant.

... Victoria Street, E.C.

Approved—ARTHUR R. LING,
GEORGE SENTER,
C. K. TINKLER.

Q*

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions ...				612	0	0
,, Admission Fees ...				1104	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1919 ...	232	0	0			
,, during 1919 ,, ,, ...	5211	0	0			
,, ,, ,, ,, 1918 ...	378	0	0			
,, ,, ,, ,, 1917 and previous ...	64	0	0			
	5885	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet ...	460	0	0			
	5425	0	0			
Add Arrears at date: 1919, £388; 1918 and previous, £390, estimated *to realise as per Balance Sheet* ...	*270*	*0*	*0*	5695	0	0
,, Lady Subscribers ...				12	0	0
,, Investments:—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...	182	11	3			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock ...	22	1	0			
,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock ...	31	18	8			
,, £1400 India 2½ per cent. Stock ...	27	2	6			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	42	0	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock	76	12	11			
,, £1200 Leeds Corporation 3 per cent. Debenture Stock ...	25	4	0			
,, £1500 Transvaal 3 per cent Guaranteed Stock, 1923/53	38	5	0			
,, £1200 North British *Railway 3* per cent. *Debenture* Stock ...	25	4	0			
,, £700 Canada 3½ per cent. Stock 1930/50 ...	19	12	0			
,, £7200 5 per cent War Stock and War Bonds ...	307	1	2			
,, £500 4 per cen Funding Loan, 1960-90 ...	5	15	11			
Income Tax Recovered ...	189	10	6			
,, *Interest on Deposit Account* ...	*26*	*4*	*6*	1019	3	5
Publication Sales:—						
Journals ...	2048	14	3			
Proceedings ...	20	19	2			
Collective Index ...	80	4	8			
Library Catalogue ...	1	16	11			
Atomic Weight Tables ...	1	13	9			
Annual Reports on Progress of Chemistry ...	320	5	0			
Memorial Lectures ...	5	18	3			
Jubilee Volumes ...	*0*	*5*	*0*			
	2479	17	0			
Less Publishers' Commission ...	241	9	7	2238	7	5
,, Proceeds of Advertisements in Journal ...	1015	1	6			
Less Commission ...	66	6	11	48	14	7
,, Miscellaneous Receipts ...				26	1	2
,, Subscriptions from other Societies ...				42	0	0
,, Donations to Library ...				40	15	0
				£11,838	1	7

FOR THE YEAR ENDED 31ST DECEMBER, 1919.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal:—						
Salary of Editor, including Indexing	620	0	0			
Salary of Sub-Editor and Assistant	250	0	0			
Editorial Postages	23	0	9			
Abstractors' Fees	393	9	10			
Printing of Journal	4625	2	7			
Banding	147	18	0			
Printing of Advertisements	296	14	9			
Wrappers and Addressing	8	3	10			
Distribution of Journal	678	16	6			
Authors' Copies	186	15	5			
Insurance of Stock	16	4	0			
				7246	5	8
Anniversary Dinner				32	16	11
Annual Reports on the Progress of Chemistry				542	15	2
Purchase of back numbers of Journal				15	14	6
List of Fellows				245	12	7
Library Expenses:—						
Salaries	639	15	6			
Books and Periodicals	259	14	2			
Binding	50	6	6			
				949	16	2
Indexing for International Catalogue				30	0	0
Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological	10	0	0			
Donation to Board of Scientific Societies	5	5	0			
Federal Council for Pure and Applied Chemistry	12	0	0			
Middlesex Hospital	5	5	0			
				32	10	0
Administrative Expenses:—						
Salary of Staff	685	11	6			
War Bonus	435	6	11			
Wages (Commissionaire, Housekeeper, and Charwoman)	288	12	2			
Coal and Lighting	88	10	5			
House Expenses and Repairs	105	18	8			
Tea Expenses	50	5	10			
Insurances	17	2	0			
Accountants' Charges	21	6	0			
Commission on Recovery of Income Tax	9	9	6			
Miscellaneous Printing	191	0	1			
Stationery	157	9	10			
Postages	122	4	1			
Advertisements of Meetings	10	16	6			
Miscellaneous Expenses	41	19	9			
				2220	7	4
Balance, being excess of Income over Expenditure carried to Balance Sheet				522	3	3
				£11,888	1	7

Research Fund Income and Expenditure Account for the Year ended 31st December, 1919.

Income.

	£	s.	d.	£	s.	d.
To Dividends on:—						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	28	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	119	7	0			
£1084 Great Western Railway 2½ per cent. Debenture Stock	18	1	10			
£1142 16s. New South Wales 3 per cent. Stock...	29	2	10			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	23	11	4			
£1365 Midland Railway 2½ per cent. Debenture Stock ...	23	17	8			
£800 Victoria 3 per cent. Stock	16	18	6			
£4498 11s. 0d. 5 per cent. War Loan, 1929-47	224	18	6			
£300 5 per cent. National War Bonds, 1928	9	16	0			
				493	13	8
,, Proceeds of Sale of Platinum and Gold				91	0	10
,, Repayment of Grants				96	15	7
,, Income Tax Recovered				33	14	7
				£715	4	8

Expenditure.

	£	s.	d.
By Grants	358	0	0
,, Commission on Recovery of Income Tax	4	13	9
,, Advertisements	2	17	0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet	349	19	11
	£715	4	8

Secretaries.—James Charles Philip, O.B.E., M.A., D.Sc., Ph.D.; Henry Rondel Le Sueur, D.Sc.

Foreign Secretary.—Arthur William Crossley, C.M.G., C.B.E., D.Sc., F.R.S.

Ordinary Members of Council.—Arthur John Allmand, M.C., D.Sc.; Edward Frankland Armstrong, D.Sc., Ph.D.; Julian Levett Baker; Francis Howard Carr; Alexander Findlay, M.A., D.Sc., Ph.D.; Francis Ernest Francis, D.Sc., Ph.D.; John Addyman Gardner, M.A.; John Millar Thomson, LL.D., F.R.S.; James Colquhoun Irvine, D.Sc., Ph.D., F.R.S.; Charles Alexander Keane, D.Sc., Ph.D.; Sir Robert Robertson, K.B.E., M.A., D.Sc., F.R.S.; Edward William Voelcker.

PRESIDENTIAL ADDRESS.

Delivered at the Annual General Meeting, March 25th, 1920.

By Sir James J. Dobbie, M.A., D.Sc., LL.D., F.R.S.

The War and Key Industries, with special reference to the Fixed Nitrogen Industry.

It is my privilege to address you for the first time as President in the year in which the war has been declared officially at an end. Whether the peace which we have achieved is to usher in a new era of greatness and prosperity for our country or to mark the beginning of its decline will depend on the thoroughness with which we have learned the lessons of the great war and with which we are prepared to apply them.

Amongst these lessons there is none more important than that which concerns the dependence on foreign countries of home industries that are vital to the safety of the State. The war has taught us that a sound national policy requires us in future to produce or have the means of producing within our own country many articles which formerly we obtained exclnsively from abroad. From a general survey of our industries it will be seen that they form a highly complex system in which certain products are essential to the manufacture of others. When these essential products cease to be available the industries dependent on them are necessarily brought to a standstill. Industries which are in this way essential to others are now commonly known as "key" industries, one of the many terms to which the war has given birth or at any rate to which it has given wide currency for the first time. When such industries are carried on exclusively abroad it is obvious that the existence of the industries in this country which depend on them must be jeopardised in time of war, and we have had many illustrations of this danger in the course of the last five years. On the outbreak of war it was discovered that we were entirely dependent on enemy sources for certain kinds of optical glass used in the construction of instruments required for war service, and the manufacture of such instruments was in consequence seriously interfered with. Again, the failure of the usual

lies of coal-tar dyes threatened a large section of our textile stries with ruin. So alarming was the position thus created the Government speedily realised the necessity for interven-, and under its ægis and with its financial assistance the move-t which now promises such rich results was inaugurated for the val in this country of the manufacture of coal-tar dyes. The gnition by Government that it is the duty of the State, in such umstances as I have described, to intervene, is perhaps one of most significant and far-reaching consequences of the war so as our industries are concerned. Many difficult and delicate nomic questions will undoubtedly arise in the future in con-xion with "key" industries, and it is important that claims the special treatment of these should be put forward only where me truly national interest is at stake.

The publication of the Report of the Nitrogen Products Com-ittee of the Munitions Inventions Department has recently rected attention prominently to the group of industries concerned ith the synthetic production of ammonia, nitric acid, and other mpounds of nitrogen. It is unnecessary for me to dwell on he importance of these compounds in their relation especially to griculture and to the manufacture of munitions of war. Without hem our agriculture would languish, and we should lack the means of producing those explosives which are most essential to the conduct of modern warfare. Yet before the end of the war our supply of ammonia was running short, and our stock of sodium nitrate could only be replenished with ever-increasing difficulty.

The Report of the Nitrogen Products Committee closes with the following observation:

"As far as the United Kingdom is concerned, nitrogen-fixation and allied processes will constitute a new 'key' industry."

This conclusion is one of enormous importance to our country, and I have thought it might be useful this afternoon to examine briefly the grounds on which it is based and endeavour to emphasise some of the lessons which may be learned from the Committee's Report.

Before the war there was no nitrogen question in this country. We were then producing about five times as much ammonium sulphate as we required for our own use, and our production was increasing at a greater rate than our consumption. In such circum-stances there seemed to he no cause for anxiety with regard to the future.

The main facts relating to the supply and disposal of the various forms of fixed nitrogen are simple, and as they are essential to a proper understanding of the nitrogen problem it will be convenient

to state them at once. We depend for ammonia almost entirely on the by-products of the gas works and coke ovens, and for sodium nitrate on our imports from Chile. Taking the average of the years 1911–13 our annual production of ammonium sulphate (25 per cent. NH_3) was 393,927 tons, of which we retained only 70,454 tons for our own use, exporting 323,473. Our average annual imports of sodium nitrate for the same period amounted to 130,997 tons.

In discussions relating to our nitrogen resources we are concerned not so much with the amounts of the various compounds containing nitrogen as with the total amount of the element. It is convenient, therefore, to express all quantities whether of ammonium sulphate, sodium nitrate, or cyanamide, in terms of nitrogen, and this plan has been followed with great advantage throughout the Committee's Report. In one of the tables entitled "Nitrogen Balance Sheet for the United Kingdom" the amount of combined nitrogen produced in this country or imported into it is shown on one side of the account, and the amount used in its industries or exported, on the other. It appears from this statement that for the period 1911–13 we produced annually on the average 82,404 tons and imported 23,979 tons of combined nitrogen, and that we exported 71,490 tons, retaining in the country for our own needs 34,893 tons. Although we are not concerned for the present with the disposal of the balance remaining in this country, it may be interesting to notice in passing what became of it. Agriculture absorbed by far the larger part—25,015 tons; the manufacture of sulphuric acid and explosives for mining and quarrying, 2885 and 1901 tons respectively; the manufacture of nitric acid, potassium nitrate, munitions of war, and fireworks together 2059 tons; the ammonia-soda and cold-producing industries, 1150 tons, leaving 1883 tons unaccounted for.

At first sight the position of Germany at the beginning of the war in regard to combined nitrogen does not seem to have differed much from our own. She obtained ammonia almost entirely from her gas works and coke ovens, but required nearly all she produced for her own purposes. Her margin for exportation in 1913 amounted to no more than 76,000 tons of sulphate. She drew her supplies of sodium nitrate, as we did, from Chile, but in consequence of the large extent of land under cultivation and her liberal use of nitrogenous fertilisers, her demand for nitrate was more than six times as great as ours, and in 1913 exceeded 800,000 tons.

When we look more closely we see that the positions, however similar superficially, differed profoundly. For some years prior to 1914 Germany had been manufacturing cyanamide on a limited scale, and not long before the outbreak of war the Haber process

producing ammonia by the direct union of hydrogen and ogen had reached the stage at which its success as an industrial ess was assured. She also possessed in the process which bears wald's name the means of converting ammonia by oxidation nitric acid. Thus there existed potentially in Germany the ans of producing unlimited quantities of ammonia and nitric d, whilst our supplies of ammonia were restricted by the output our gas works and coke ovens, and we were entirely dependent nitric acid on the importation of sodium nitrate. So far as se commodities, so necessary to her agriculture and to the con- ct of the war, were concerned, Germany was self-contained and s in a position to supplement the ammonia which she obtained om by-product sources and to replace the sodium nitrate which e imported from overseas to any required extent by synthetic oducts. Although exact statistics are not obtainable, it is esti- ated that her production of calcium cyanamide, which was only 1,000 tons in 1913, had risen in 1917 to at least 400,000 tons, and ithin the same period her production of ammonium sulphate by he Haber process had increased from 30,000 tons to 500,000 tons. 'he development of the ammonia oxidation process in the course f the war was a still more remarkable achievement when it is emembered that it had only been tested on a comparatively small ndustrial scale when the war began. There is good reason to believe that by the middle of 1916 the amount of sodium nitrate produced by Ostwald's process was equivalent to more than a quarter of a million tons of nitric acid per annum.

The synthetic production of nitric acid was a necessity for Germany. By our blockade she was cut off from her overseas supplies of sodium nitrate, and had she been unable to make good the want from internal sources she would have been compelled to sue for peace as soon as her reserve stocks were exhausted. The development of the ammonia oxidation process alone made the war possible. It has been well said that this was a chemists' war.

As the war progressed it was not long before the weakness of our position became apparent. We have seen that at its commencement our production of ammonia was far in excess of our own requirements, and after our Navy had swept the German cruisers from the seas there seemed to be no longer any ground for anxiety as to the maintenance of our supplies of sodium nitrate. With the development of the submarine warfare, however, a new situation was created. The importation of nitrate was again endangered, and although we had still sufficient ammonia available to give us by oxidation all the nitrate we required, we possessed neither the plant nor the technical experience necessary to effect

the conversion. The sodium nitrate that continued to reach us was required to an ever-increasing extent for the manufacture of munitions, and soon there was none available for agriculture, and it was necessary to replace it for this purpose by ammonium sulphate. The substitution of ammonium sulphate for sodium nitrate as a fertiliser made a further heavy demand on our surplus stock of the sulphate. This was also being more and more depleted by the ever-growing requirements of the munition factories, especially after the introduction of amatol, which contains as much as 80 per cent. of ammonium nitrate, and it became necessary to restrict the exportation of ammonium sulphate. The amount exported, which reached 325,000 tons in 1913, fell in 1916 to 259,000 and in 1918 to 19,150 tons, but even this did not long suffice to allay anxiety with regard to the future. With the increasing destruction of our corn ships, the question of maintaining our food supplies became one of great urgency. Steps were taken to increase the area of cereal cultivation and at the same time to increase by heavier manuring the productivity of the land already under the plough. These measures made still further demands on our stock of ammonium sulphate, and it was recognised that the time was rapidly approaching when the ample margin existing at the beginning of the war would be exhausted and the country would be face to face with a shortage of ammonia. Before the war ended the shortage was actually making itself felt. According to a statement made to the Committee on behalf of the Board of Agriculture, 60,000 tons of ammonium sulphate more than was available could have been disposed of to farmers during the season June, 1917, to May, 1918.

Thus a situation had actually arisen which, had it been suggested at the beginning of the war, would have seemed too remote for serious consideration.

We know now that under the conditions of modern warfare we are exposed to a formidable danger against which we can only adequately protect ourselves by having at command the means of producing ammonia and nitric acid to any required amount within our own shores. This is the inevitable conclusion that is forced upon us by a study of the facts as they unfolded themselves in the course of the war.

Already in the early summer of 1916 the position was causing so much anxiety that with the sanction of the present Prime Minister, then Minister of Munitions, the Committee, afterwards known as the Nitrogen Products Committee, was appointed to report on the whole question of the fixation of atmospheric nitrogen, with reference to the needs of the country and the Empire,

on the steps necessary to conserve and increase the national urces in nitrogen-bearing compounds. Although by the terms eference the scope of the Committee's inquiry extended to peace well as to war conditions, the question that pressed for an nediate answer was how to increase our supply of ammonia, if essary, during the war. Obviously one of the first steps was to amine into the possibilities connected with the existing sources supply. The Committee, therefore, instituted an exhaustive quiry into the conditions of the various industries in which monia is obtained as a by-product. Improvements in the existg practice of recovery from the gas works; the saving of the nmoniacal liquor which is at present allowed to run to waste from e smaller works; the replacement of the beehive ovens still extenvely used in this country in coke-making by ovens adapted to e recovery of the ammonia produced in the process; the more xtended use of coal gas and coke instead of raw coal for domestic nd industrial purposes, were all considered, and suggestions under hese various heads were made to the Ministry of Munitions. It vas, however, clearly established that whilst a substantial increase f ammonia might ultimately be obtained from such sources, the mmediate gain could not be great. As a matter of fact, the yield of by-product ammonia in this country increased by 26,000 tons between 1913 and 1917, the increase being due mainly to the substitution of recovery for beehive ovens.

Possible sources of supply not hitherto utilised, such as peat and sewage, were also reviewed, but no satisfactory method of obtaining ammonia from them on the industrial scale having yet been worked out, it was recognised that extensive investigation, probably extending over a long period, would have to be undertaken before the practicability of utilising them economically as sources of ammonia could be put to the proof.

It remained to inquire into the possibility, as a war measure, of installing one or other of the processes for the fixation of nitrogen which were in use on the Continent. Two things had to be considered in this connexion: the suitability of the various methods to the conditions of this country, and the time likely to be required for their installation, having regard, amongst other things, to the amount of preliminary experimental work involved. It was obvious that those processes which depend on the direct union of oxygen and nitrogen under the influence of the electric arc are unsuited to this country owing to the want of a cheap and abundant supply of water-power to produce the large amount of electric energy required. The production of calcium cyanamide, from which ammonia is readily obtained, also requires a large expendi-

ture of energy, although a relatively small amount per unit of nitrogen fixed, as compared with the arc processes. This, however, is counterbalanced to some extent by the abundance and cheapness of the limestone and anthracite required for its production.

Although cyanamide had never been manufactured in this country, the working details of the process were easily procurable, and the Committee felt justified, therefore, in recommending it for adoption as the one best suited to meet any shortage of ammonia that might occur during the war. This recommendation was at first adopted, but for reasons which I need not enter into now was not acted on.

From the date of the appointment of the Committee a staff of chemists and physicists, under the direction of Dr. J. A. Harker, was actively engaged in an experimental investigation of the conditions of the manufacture of ammonia by the Haber process, which had been introduced into Germany not long before the outbreak of war. This process requires the expenditure of only a comparatively small amount of power, and is therefore well adapted to the conditions of this country. It is simple in theory, consisting in the direct union of nitrogen with hydrogen in the presence of a catalyst at a high temperature and pressure. Those, however, who recall the lecture delivered by Haber at Liverpool in the early part of 1914 will appreciate the magnitude of the physical and mechanical difficulties that had to be overcome before the process attained technical success. Unfortunately, the working details were unknown to our chemists, and had to be studied experimentally both from the chemical and the engineering point of view. The selection of a suitable catalyst, the conditions under which it acts most efficiently, the effect of impurities, the conditions of temperature and pressure, the influence of the rate at which the gas passes through the apparatus upon the yield of ammonia, the best method of removing the ammonia produced, the physical problems connected with the circulation of gases at high pressures and velocities, were all subjected to systematic investigation. Moreover, the difficult problem of making provision for an abundant supply of cheap and pure hydrogen, which is indispensable to the process, had to be worked out at the same time. The new developments during recent years in the manufacture of hydrogen on a large scale for the hydrogenation of fats and oils, as well as for aviation purposes, give a special interest to the researches, carried out for the Committee, on catalytic processes for hydrogen production and purification.

These investigations were begun in the summer of 1916, and the results obtained by the beginning of the following year were con-

dered so promising that the Committee included in an interim report submitted to the Ministry of Munitions in February a recommendation for the erection of a trial plant. They were not, however, then prepared to put forward proposals for the establishment of the Haber process on an industrial scale. In October, 1917, however, the Explosives Department of the Ministry of Munitions felt justified by the results of the experimental work obtained by that date in recommending that this process should be adopted as the basis of a national factory for the production of fixed nitrogen, and the erection of a factory was actually in progress when the war ended.

Much successful experimental work had also been carried out on the oxidation process for the conversion of ammonia into nitric acid and ammonium nitrate, and it was proposed to include plant for these purposes in the national factory.

In the course of the experimental work carried out for the Committee many interesting and valuable observations were made and many important results, both from the scientific and technical point of view, were obtained. When the reports describing the investigations are published they will be found to constitute an addition of great value to the scientific and technical literature of the subject, and will form a lasting memorial to the skill and energy of the chemists and physicists who took part in them. Although no doubt something remained to be done on the engineering side, the fact that they should have succeeded in so short a time in bringing a process, which it cost the Germans so much time, trouble, and money to perfect, to the stage at which it was deemed fit for adoption by the Ministry of Munitions, was surely a notable achievement.

In this connexion I may perhaps be allowed to refer to the death of Dr. *Harold Greenwood*, a *Fellow of this Society*, who *had* charge from the beginning of the investigation of the synthetic ammonia problem, and whose exceptional ability and untiring energy contributed so largely to the important results obtained.

I have now traced the causes which led, as the war proceeded to the gradual absorption of the surplus of ammonia which w produced in excess of our own needs in pre-war days, and I hav described the action which was taken to meet the shortage whic had actually begun to make itself felt in the course of the war.

If I have succeeded in making the position clear, you wi realise that at the close of the war we were rapidly approaching crisis as regards our supplies of combined nitrogen. Our hu surplus of ammonia had gone, and the demands of the muniti factories and of agriculture were ever on the increase. On t

other hand, the importation of sodium nitrate was carried on under great difficulties, and the usual sources of our ammonia supplies were found to be incapable of any considerable expansion. In these circumstances surely the conclusion of the Committee is justified that nitrogen-fixation constitutes a "key" industry which is essential to our economic safety and to our national defence, and that it is one of those industries which should be established, if necessary, with the assistance of Government. In time of war complete independence of external supplies of combined nitrogen is a necessary condition of safety, and independence can only be secured if we have within the country the means of producing fixed nitrogen to any extent that may be required. Our potential sources of by-product ammonia are undoubtedly very large, but the practicability of making use of some of them has yet to be demonstrated, and the extent to which some of those which are known to be capable of utilisation can be made immediately available is very limited. On the other hand, although the processes for producing fixed nitrogen have not yet been established in this country, their installation could be quickly effected, and we should then be possessed of the means of indefinitely increasing our nitrogen production. To ensure the safety of the country, however, it is sufficient in the opinion of the Committee that we should possess experience of the working of the fixation processes and nucleus plant which would be capable of rapid extension.

Apart from the question of security in time of war, there are other reasons which render it in the highest degree important that the synthetic processes for the production of nitrogen compounds should be established in this country. The demand for combined nitrogen for purposes other than the manufacture of munitions of war is greater now than before the war, and is certain to expand still further. This is due to a variety of causes, but mainly to the increased requirements of agriculture. Our pre-war consumption of artificial nitrogenous manures of all forms was only equivalent to 25,000 tons of nitrogen. Towards the end of the war it had risen to 60,000 tons in consequence of the addition of nearly 4,000,000 acres to the land under the plough, and to the more intensive cultivation resorted to with the object of increasing the production of the soil. Unless we have already forgotten one of the lessons of the war we must continue to grow a larger proportion than formerly of the grain we require, and unless the money spent on agricultural education has been spent in vain we must expect an ever-increasing demand for artificial fertilisers. Assuming that the present acreage now under the plough is maintained and that nitrogenous manuring on a moderate scale is more gener-

ally resorted to, Dr. E. J. Russell estimates that eventually the equivalent of half a million tons of ammonium sulphate, or 100,000 tons of combined nitrogen, will be required annually for fertilising purposes alone. This increase might, no doubt, be met partly by increased importation of sodium nitrate, but, since our agriculture requires both forms of fertiliser, a large additional amount of ammonium sulphate must be obtained from some new source of supply or taken from what is at present available for exportation.

The maintenance of our export trade is of vital importance to the country, especially in present circumstances, but it is clear that we cannot both continue to export ammonium sulphate on the pre-war scale and meet the growing demands at home unless we increase our production of ammonia. In this connexion it is to be remembered that during the war Germany was manufacturing nitrogen products far in excess of her peace requirements, and that, with the plant now set free, she is probably in a position to compete with this country and with Chile in the nitrogen markets of the world. How far she will be able to do so successfully will depend on economic factors which are at present unknown. It is certain, however, that under pre-war conditions synthetic nitrogen compounds could be produced at prices which compared favourably with those at which ammonium sulphate and sodium nitrate were then sold. Should this still hold good, our export trade will be endangered unless we are in a position to oppose British to foreign synthetic products.

Having dwelt on the difficulties and dangers which during the war threatened our industries dependent on nitrogen products, it is satisfactory to be able to add that one of the most important recommendations of the Committee is in a fair way of being acted on.

It is generally understood that the national factory at Billingham-on-Tees, the erection of which was begun in 1918, is about to be acquired by an influential syndicate representing a large proportion of the heavy chemical trade of the country. It is the intention, I understand, to commence with a moderate-sized synthetic plant in which many of the details will represent notable improvements on existing German practice, and ultimately to develop this into a very large commercial project. In addition, the manufacture of nitric acid and nitrates by the oxidation process will form part of the scheme, and it will be possible to produce from this source a considerable part of the national requirements of nitric acid for commercial purposes.

Such a combination of chemical interests opens up vast possibili-

ties for the more economic production of ammonia, by combining its manufacture with other industries in which the by-products of the Haber process could be utilised. The Solvay process, for example, in which large quantities of carbonic acid are required, is stated to be already in operation in Germany in association with the Haber process. Other developments may be looked for in connexion with the disposal of the large quantity of oxygen resulting from the production of nitrogen, and this, again, may lead to the recovery in quantity of the rarer elements of the air which are now coming into demand for technical purposes.

It is important, however, not only that effect should be given to the specific recommendations of the Committee with regard to the established processes, but also that the researches begun during the war on processes still in the experimental stage should be continued. Many branches of the problem still call for investigation both in the case of the by-product and the synthetic industries.

As an instance of the former I may mention the proposal to prepare a smokeless fuel for domestic use by carbonising coal at a low temperature under conditions which would allow of the recovery of the ammonia. This problem is now being investigated by the Fuel Research Board. Another interesting subject connected with the utilisation of by-products is the treatment of coal used at electric power stations for recovery of ammonia. Here the increased amount of fuel required when the by-products are recovered as compared with the amount required in direct firing must be set against the value of the by-products. You cannot have both the full heating value of the fuel and the by-products. This is a point too often overlooked when discussing the question of our potential supplies of ammonia.

Amongst the synthetic processes still in the experimental stage, which in the opinion of the Committee should be further investigated, is the interesting Häusser process, in which the heat of explosion of a mixture of combustible gas and air is utilised to bring about the union of nitrogen and oxygen without the large expenditure of electrical energy required by the arc processes. The exhaust gases from the explosion apparatus contain oxides of nitrogen which can be recovered by absorption in water. By this process both power and nitric acid can be obtained simultaneously. From this point of view the Committee consider that it is of sufficient promise to justify the expenditure necessary for further experiments as to the practicability of the process.

It is idle to suppose that we can enter on the fixed nitrogen industries to advantage unless we are prepared to pursue an active policy in regard to them.

is satisfactory, therefore, to learn that whilst the technical engaged on the work of the Committee has been largely dis- led, and the temporary research laboratories restored to their inal purposes, the section of the staff engaged on the synthetic nonia problem has been taken over by the syndicate already rred to, and is continuing under them the investigation of e of the remaining problems. Moreover, although the Inven- is Department of the Ministry of Munitions has ceased to st, a small nucleus organisation has up to the present been ained, and is actively engaged in applying to the post-war situa- n the information and experience on the nitrogen problem lected by the Committee. I may add that at the present ment a number of important fixation schemes are in course of velopment, not only in the United Kingdom, but also in Egypt. uth Africa, Canada, Newfoundland, the West Indies, New aland, Ceylon, and India, and some of these are receiving the tive support of the Governments concerned.

My purpose in bringing this subject before you on the present casion is not only to emphasise the importance of the conclu- ons of the Nitrogen Products Committee, but to direct attention a wider question suggested by its inquiry. Our attitude towards e fixed nitrogen problem illustrates a defect in our attitude wards such problems generally. Where our individual interests re not affected we are prone to be indifferent to and to overlook evelopments in other countries which in their results may be of ital importance to us as a nation. We are thus exposed to the langer of having our economic position disturbed and our safety mperilled by the introduction of new factors of the importance, or it may be of the very existence, of which we have remained ignorant until they have made themselves felt by their conse- quences. Where particular industries are affected those who are immediately concerned can generally be trusted to look after their interests when they understand them. In matters which do not affect any special interest, however, but may yet be of the gravest import from the national point of view, there is no one to hold a watching brief for the nation.

While the fixed nitrogen industries were being rapily developed on the Continent the subject attracted little general attention in this country. As we had an abundant supply of ammonia and were able to import sodium nitrate at will, our interest in the new processes was purely academic. Yet our failure to realise their importance, and to grasp the larger aspects of the problems involved, nearly led to disaster.

I do not think we need take blame to ourselves for having

failed to realise in its full extent the peril to which we were exposed at the beginning of the war. That would have required gifts of imagination with which we as a nation are not usually credited. The complaint is that no consideration whatever had been given to the national aspects of the matter in relation either to peace or war conditions, and that no precautions had been taken against the more obvious dangers.

The first person in this conntry to direct attention prominently to the development of the fixed nitrogen industries abroad was the present Foreign Secretary of our Society. In a lecture delivered before the Pharmaceutical Society in 1910, Professor Crossley gave an account of the production of uitrogen compounds at Odda, in Norway, and pointed out the importance of the work from the national point of view. "It might naturally be expected," he said, "that the problem of the utilisation of atmospheric nitrogen should be considered as one of real and undoubted importance to the country, not only from the point of view of agriculture, but also as a means of supplying the necessary nitric acid for the manufacture of explosives. . . . Yet there do not appear to be any signs that the matter is regarded as one of national importance." Detached notices of the various methods of synthesis employed had no doubt appeared from time to time in the journals and papers at an earlier date, and in 1906 Professor Frankland, in an address to the Society of Chemical Industry at Birmingham, gave a short account of the methods that had been proposed before that date for utilising the nitrogen of the atmosphere, but Professor Crossley's lecture was, I believe, the most complete account of these new industries published in this country before the war.

In the early months of the war the nitrogen question was considered by a Committee of the Board of Agriculture, and it was soon discovered how imperfect was the information on the subject availahle in this country. This Committee sought the aid of the Chemical Society, and Dr. Scott, then President, was fortunate in obtaining the assistance, amongst others, of Mr. G. S. Albright, who afterwards rendered invaluable service as a member of the Nitrogen Products Committee, in preparing a Report on the subject for the Board of Agriculture. This report was placed at a later date at the disposal of the Nitrogen Products Committee, which commenced its sittings in the summer of 1916 and was engaged during the next three years in the long and elaborate inqniry which led to the conclusions we have been considering this afternoon.

In the course of its inquiry the Committee was constantly con-

ed with the difficulty of obtaining accurate statistical and information relating to the various industries concerned with production of nitrogen compounds. The figures on which Report is largely based had to be laboriously collected from y different sources. Much valuable information was obtained . the returns of the Chief Inspector of Alkali Works and other al sources, but in not a few instances figures which would have erially assisted the inquiry were altogether unprocurable. Thus, ake only one example, when considering the possibility of easing the supply of ammonia from by-product processes, it desirable to obtain information as to the allocation of the l consumed in this country by different industries and classes consumers, but no trustworthy figures were available on the ject. It is unnecessary to dwell further on the importance of ssing for the adoption of the strong recommendations which Committee has made on this subject to the effect that annual tistics of the nitrogen and other industries of the United ngdom should be officially collected and published.

It was, however, not statistical information only that was cking. With the exception of the lecture I have already referred , which was necessarily limited in its scope, we possessed at the ginning of the war no adequate account of the state of the trogen industries on the Continent. For that the Committee had go to a "Report on the Utilisation of Atmospheric Nitrogen," y Thomas H. Norton, American Consul at Chemnitz. This Report as issued by the Bureau of Manufacturers of the Department of Commerce and Labour of the United States in compliance with n Act of Congress of 1911 authorising investigations of trade onditions abroad. It contains a large amount of valuable informaion regarding the experimental details and industrial prospects of he various fixation processes which had either achieved success or were still in the experimental stage when the Report was compiled in 1912. Although it had no special reference to the conditions in this country it was nevertheless of the greatest use to the Committee as affording a comprehensive survey of the position of the fixed nitrogen indnstries on the Continent shortly before the war.

Amongst the officers of his ideal State, "The New Atlantis," Bacon included twelve whose duty it was to sail into foreign countries and bring back the "books and abstracts and patterns of experiments of all other parts." These he called "Merchants of Light." We, too, have need of our Merchants of Light. Is it

too much to hope that some effective combination of the Departments concerned with the technical and scientific work of the nation may yet be devised for the purpose of keeping us in close touch with new developments abroad with which it is desirable in the interests of the State that we should be acquainted?

OBITUARY NOTICES.

SIR WILLIAM CROOKES, O.M.*

BORN JUNE 17TH, 1832; DIED APRIL 4TH, 1919.

THE author of a succession of papers published by the Royal Society and other scientific bodies extending over sixty-seven years (from 1851 to 1918), to say nothing of a number of technical treatises in the form of large volumes, must have been a man of remarkable industry as well as intellectual qualities, and those who believe in the influence of heredity will therefore be disposed to look for some indication of the ancestral origin of these qualities in the famous man who has so recently passed away.

His father, Joseph Crookes, born in 1792, the son of a small tailor in the north of England, came to London a poor boy. He was evidently a man of brain and energy, for the tailor's business he established proved so prosperous that when he died in 1884, at the age of ninety-two, he was a rich man. Joseph Crookes married on February 24th, 1831, at Aynhoe, Northamptonshire, as his second wife, Mary Scott, and from this lady he had a second family of several sons and daughters. William was her firstborn, and resembling her in feature and in disposition, it may be surmised that he derived some of his characteristics from her.

There is but little to say concerning William Crookes's early years. Improbable as it may appear, he always maintained that he remembered learning to stand and to walk. Such regular education as he received was obtained at a grammar school at Chippenham. His father wished to make him an architect, but in the end he satisfied his inclination for experimental work, already indicated at home, by entering the Royal College of Chemistry under Hofmann, the first professor, in 1848. He must have made extraordinary progress, as in 1851 his first paper appeared in three

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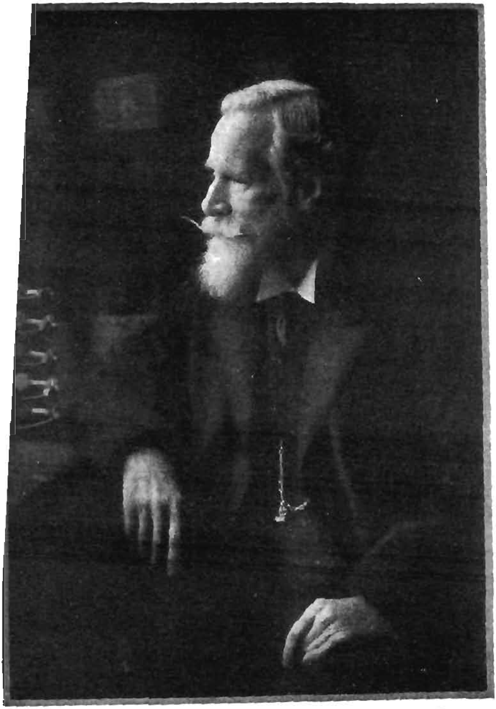


William Crookes.

[*To face Trans., p.* 444.

German chemical journals to which it was communicated, doubtless by Hofmann. The English version was printed in the *Quarterly Journal of the Chemical Society* (1852, **4**, 12), "On the Selenocyanides, by William Crookes, Esq., Assistant in the Royal College of Chemistry." This position as assistant he retained from 1850 to 1854. He then went to Oxford for a short time as Superintendent of the Meteorological Department at the Radcliffe Observatory, and in 1855 he became Lecturer on Chemistry at the Chester Training College.

In 1856 he married Miss Ellen Humphrey, a native of Darlington, whose acquaintance he had made some years earlier as a school friend of his cousin. They were married on April 10th, 1856, at the Parish Church of St. Pancras, Middlesex, and began housekeeping at Brompton. They removed to 20, Mornington Road, N.W., and afterwards to 7, Kensington Park Gardens in 1880, and this was their home to the end of their lives. In 1859 he brought out the first number of the *Chemical News*, of which he remained sole editor until 1906.

In the meantime he seems to have been much occupied with the study of phenomena connected with the nature and effects of light, for several papers relating to photography were published between 1853 and 1857. Soon after this, the employment of the prism in recognising and distinguishing volatile substances in flame was introduced by Bunsen and Kirchhoff, and the discovery of rubidium and cæsium in the water of the Dürkheim spring was announced by Bunsen in 1860. On applying the spectroscope to the seleniferous material from the vitriol works at Tilkerode (Harz), which had been given to him by Hofmann some years previously, and which he had used as the source of selenium in his work on the selenocyanides, Crookes observed a new green line which led him to the discovery of thallium. The first announcement of the existence of a new element appeared in the *Chemical News*, March 30th, 1861. It was originally supposed to be related to sulphur, but the discoverer soon saw fit to alter his opinion, and the specimens exhibited in the International Exhibition, 1862, and to which a medal was awarded, were labelled Thallium, *a new metallic element*. The discovery was interesting from several points of view. The use of the spectroscope was novel and the properties of the new metal were strange, exhibiting as it does the appearance and approximately the density of lead, some of its salts resembling those of lead and mercury, whilst others are perfectly similar in solubility and crystalline relations to the salts of the alkali metals. The discovery of thallium at once secured for William Crookes a recognised position in the scientific world, and in 1863 he was

elected F.R.S. Obviously the first task which lay before him was the investigation of the chemical and physical properties of the new element and its sources in nature. Among the most important of the physical constants to be determined was the atomic weight, and the remarks on the subject contained in Prof. F. W. Clarke's "Constants of Nature" (Smithsonian Institution, 1882) may properly be quoted here. "In 1873, Crookes, the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities of absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed specially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly *in vacuo*, but all were reduced to *absolute* standards, and unusually large quantities of thallium were employed in each experiment. . . . Suffice it to say that the research is a model which other chemists will do well to copy. . . . Hence, using the atomic weights and probable errors previously found for N and O, $Tl = 203{\cdot}715 \pm {\cdot}0365$. If $O = 16$, $Tl = 204{\cdot}183$. . . . Crookes himself, using 61·889 as the molecular weight of the group NO_3, gets the value $Tl = 203{\cdot}642$; the lowest value in the series being 203·628 and the highest 203·666, an extreme variation of 0·038. This is extraordinary accuracy for so high an atomic weight, at least as far as Crookes's work is concerned."

This passage illustrates the spirit which animated Crookes's work throughout. Nothing short of the highest attainable accuracy ever satisfied him.

The use of the vacuum balance, however, was attended by unexpected phenomena, which occupied his attention for many years afterwards and led to the discovery of the *radiometer* in 1875. This was described in a paper entitled "On Attraction and Repulsion resulting from Radiation," communicated to the Royal Society on March 20th, 1875. A Royal Medal was awarded to Crookes at the Anniversary Meeting in the same year. The President in presenting the medal referred to the instrument in the form in which it has been since familiar, namely, with the four-armed fly mounted on a sharp point and having the vertical disks at the ends of the arms blackened on one side. He also remarked, "it is the mystery attending this phenomenon that gives it its great importance." Great interest was manifested by many experimenters in the phenomena observed, and there were many attempts at explanation. In the end, the hypothesis put forward by Dr. G. Johnstone-Stoney, according to which the repulsion is due to the movements of the molecules of the residual gas acting

differentially on the two surfaces of the movable disk, was accepted.

In a footnote to one of his papers (*Proc. Roy. Soc.*, 1876, **25**, 308), Crookes drew attention to the properties of highly attenuated gas, and expressed the view that the phenomena indicate the existence of a fourth state of matter as far removed from the condition of gas as gas is from liquid.

In all the numerous experiments connected with this investigation, Crookes was assisted by Mr. C. H. Gimingham, whose mechanical dexterity and skill as a glass-blower were quite remarkable. Gimingham joined the Swan Electric Light Company in 1881, but unhappily died a few years later.

The phenomena exhibited by the electric discharge in rarefied gas had long been familiar, and had been studied by Plücker, by Hittorf, and other physicists. It was natural that in the examination of the properties of highly attenuated gas the phenomena exhibited by electric discharge through such media should receive Crookes's attention, and in the paper in which his first experiments in this direction were described (*Proc. Roy. Soc.*, 1879, **28**, 110), he was led to theoretical speculations on the ultra-gaseous state of matter. In this paper, the dark space which appears round the negative pole was the subject of experiment, and was found to enlarge as the exhaustion proceeds, whilst the phosphorescence excited on the glass walls of the tube diminishes and ultimately disappears. The dark region round the electrode has since been known as the *Crookes*, or *cathode dark space*. The rays from the cathode may be made to converge by the use of an aluminium cup, and the result is the production of a green phosphorescent spot on the glass; the rays, travelling in straight lines, cast a strong shadow from any object placed in their path. The rays when concentrated also develop great heat, which may rise to the melting point of platinum.

In 1880 the French Académie des Sciences awarded Crookes an extraordinary prize of 3000 francs and a gold medal in recognition of his discoveries in molecular physics and radiant matter. In the years following 1880 he continued the active investigation of the phenomena exhibited by gases in a highly attenuated state, and among other properties he studied the heat conduction and viscosities of gases in this condition. He also examined the phosphorescence exhibited by many substances when exposed to the discharge from the negative pole in a highly exhausted tube; and in the Bakerian Lecture for 1883, speaking of this discharge as "radiant matter," he considered that the particles flying from the cathode were of the dimensions of molecules.

For some years he was occupied in tracing by the spectroscope the changes noted, and he was led to attempt the separation of some of the earths, notably yttria, into the components of which they were supposed to consist, by means of a very elaborate system of chemical fractionation. The result of all this work led him to speculations as to the characters of the elements and the existence of a class of bodies which he called "meta-elements." These meta-elements he regarded as composed of atoms "almost infinitely more like each other than they are to the atoms of any other approximating element. It does not necessarily follow that the atoms shall all be absolutely alike among themselves. The atomic weight which we ascribe to yttrium therefore merely represents a mean value around which the actual weights of the individual atoms of the 'element' range within certain limits. But if my conjecture is tenable, could we separate atom from atom we should find them varying within narrow limits on each side of the mean." This view was put forward in the Presidential Address to the Chemical Society, 1888, the whole of which even now, after thirty years, would repay perusal. The possibility of the evolution of the elements from a primal elementary protyl or urstoff is a proposition which has been discussed from the most ancient times, but the chemist had little positive information as to the inter-relations among the recognised elements before the conception of the periodic law. Taking an idea from Prof. Emerson Reynolds for the diagrammatic display of the periodic relation of properties to atomic weight, Crookes produced a figure of eight curve, on which the symbols of the elements are placed at intervals so that the members of natural families fall into position vertically over one another.

On this curve the meta-elements would be ranged in groups or clusters close together. Radioactivity had not been discovered when this address was composed, but something approaching Crookes's idea has been realised in more recent times by the discovery of isotopes among the products of the disintegration of radioactive elements. For his researches on the behaviour of substances under the influence of the electric discharge in a high vacuum, with special reference to their spectroscopic behaviour, the Davy Medal was awarded to Crookes by the Royal Society in 1889.

The discovery of argon by Rayleigh and Ramsay in 1894, and of helium by Ramsay in 1895, opened a new field, and Crookes being recognised as the most experienced observer of spectra and the highest English authority in this direction, the new gases were

at once submitted to him, and the identity of terrestrial with solar helium was established finally by his examination.

Soon after this time the brilliant researches of J. J. Thomson threw an entirely new light on all the difficult spectroscopic questions which had been so patiently and so successfully examined by Crookes. It became clear that the particles projected from the cathode were much smaller than any known atoms or molecules of ordinary matter, and were, in fact, the minute bodies called electrons. On this point, Crookes in a paper on the "Stratifications of Hydrogen" (*Proc. Roy. Soc.*, 1902, **69**, 411), expressed himself in the following terms: "In twenty-five years one's theories may change, although the facts on which they are based remain immovable. What I then called 'Radiant Matter' now passes as 'Electrons,' a term coined by Dr. Johnstone-Stoney to represent the separate units of electricity which is as atomic as matter. What was puzzling and unexplained on the 'Radiant Matter' theory is now precise and luminous on the 'Electron' theory." And by application of this theory the stratifications of hydrogen were explained.

The discovery of radioactivity by Henri Becquerel and of radium by Madame Curie towards the end of the century naturally attracted Crookes's interest and attention. On examination of uranium salts, some specimens were found to be much more radioactive than others. It was soon found that the radioactive constituent is precipitated from a solution by ammonia, and on adding excess of the reagent, a small, insoluble, light brown precipitate is left which exhibits strong radioactive properties, whilst the uranium salt remaining is almost inactive. A year later the uranium had regained its activity. To the active substance the name uranium-*X* was given. Whatever be its nature, it is evident that uranium owes its usual activity to the presence of this substance which is generated from it, and the separation of which depends on the readiness with which it attaches itself to precipitates, especially ferric hydroxide, when iron is present as an impurity in the uranium compound employed as material. The year following, Crookes, continuing his observations on the emanations of radium, discovered the effects produced by the α-rays on a surface of hexagonal blende (zinc sulphide), and invented the little instrument, which he called the spinthariscope, by which the number of scintillations can be counted, each spark being produced by one α-particle.

The researches on the spectra and other characters of the rare earths occupied more than twenty years, and one result was a very

extensive study of scandium and its salts, which places it in the position of being now better known than almost any other of these difficult elements from which scandium is separated by its low atomic weight.

In 1908 Crookes drew attention to the remarkable resistance to the attack of all kinds of reagents by the metals iridium and rhodium, and in 1912 he recorded a useful series of observations on the relative volatility of metals of the platinum group. In the case of platinum at 1300°, the metal seems to volatilise *per se*, whereas the loss of weight of iridium is probably due to the formation of a volatile oxide. The spectra of elementary boron and silicon were the subjects of papers communicated to the Royal Society in 1912 and 1914.

A very valuable investigation undertaken in connexion with the Glass Workers' Cataract Committee of the Royal Society was begun in 1909. The main object was to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workpeople. This involved a study of the effects of the addition of a large number of metallic oxides to a colourless glass, specially prepared for the purpose by Mr. H. Powell, of the Whitefriars Glass Works. The problem was to prepare a glass which would cut off as much as possible of the heat radiation, and at the same time be opaque to the ultra-violet rays, whilst the colour would be scarcely noticeable when used in spectacles. In the result, a series of eighteen different recipes were provided which meet, more or less fully, the three requirements contemplated. These have been found to be, in practice, very beneficial to the workers.

We may now recall some of the subjects which at various times were studied by this untiring worker, outside the course of research which may be supposed to have represented his predilection.

It should not be forgotten that when quite a young man he was appointed by the Government to report on disinfectants and their application to the arrest of the cattle plague in 1866, and that he was responsible for the recognition of the antiseptic value of phenol or carbolic acid.

The diamond has been ever a subject of interest, not merely to the jeweller, but to the mineralogist and chemist, owing to the mystery in which, up to recent times, its origin and formation were involved. In a visit to Kimberley in 1896, Crookes spent nearly a month in the mines studying the question of the origin of the mineral, and again in 1905, on the occasion of the visit of the British Association, he pursued the same inquiry. In 1893 the late Prof. Moissan demonstrated the production of diamonds by crystallisation of carbon from molten iron under pressure, and

Crookes showed that the residue of cordite exploded in a closed steel cylinder contains crystalline particles possessing the form of the diamond. He published an interesting little book on diamonds in 1909.

Another subject in connexion with which he did good service was the importance of producing and applying to the land much larger quantities of nitrogen in the form of nitrate in order to increase the supply of wheat. "The Wheat Problem" was one theme of his Presidential Address to the British Association at the meeting at Bristol in 1898, and his views on the subject were embodied in a volume published a year later, in which he was able to reply to the various critics who in the meantime had questioned some of his conclusions. Though, doubtless, some of his most startling statements admit of modification, the problem still remains a topic of supreme interest to the agriculturist and to the world at large.

It would be almost impossible to enumerate all the various lirections in which Sir William Crookes (he received the honour of knighthood in 1897) occupied himself in connexion with problems of public interest or as expert adviser to the Government, but, in passing, may be mentioned his work on the disposal of town sewage, his reports on the composition and quality of daily samples of the water supplied to London from 1880 to 1906, and his services as Consulting Expert on the Ordnance Board from 1907 onwards during the period of the war. Nor should it be forgotten that the office of President is in many learned societies no sinecure. In presiding over the Chemical Society (1887–1889), the Institution of Electrical Engineers (1890–1894), the British Association (1898), the Society of Chemical Industry (1913), and, finally, the Royal Society (1913–14–15), Sir William paid close attention to all the multifarious details of the business of each society. He also served as Honorary Secretary to the Royal Institution from 1900 to 1913, and as Foreign Secretary to the Royal Society from 1908 to 1912. Every man of science among his contemporaries will be ready to affirm, therefore, that the numerous honours which were showered on Crookes by the most distinguished academies and universities in the world were well earned and very fittingly conferred. He received from the Royal Society the Royal, the Davy, and the Copley Medals, and from the Royal Society of Arts the Albert Medal, and finally, in 1910, the Order of Merit was conferred on him by the King.

Crookes's whole scientific career is interesting, apart from the value of his discoveries, as illustrating the fact that to a man of genius the character of his early education has but little influence

on his achievements. As mentioned already, he left school at the early age of fifteen, and at once specialised in a single branch of science under a teacher eminent in his own line, but from whom the young student seems to have derived little but the advantage of example, for the subjects to which Hofmann devoted his energies appear to have had but little attraction for Crookes. Unlike W. H. Perkin, who also entered the college at about the age of fifteen with equally imperfect general education, he never seems to have been attracted by organic chemistry, and to the end of his life remained practically ignorant of this branch of science. The genius displayed by Crookes was, however, accompanied by unusual independence of character, which was displayed in a variety of ways, not only in the course taken by his own researches, but by his attitude toward the statements and pretensions of others. Nothing seemed too improbable to escape his attention, and of this the time and trouble he was tempted to expend on the pretended transmutation of silver into gold some twenty years ago is a sufficient illustration. The same liberality of spirit made him very tolerant, and perhaps not always sufficiently critical, in regard to articles in his paper, the *Chemical News*.

Here we must add that no account of William Crookes's life as a scientific man would be complete, and less than justice would be done to his personal character and independence of spirit, if all reference were omitted to the investigations in which, early in his career, he became involved concerning the phenomena of so-called "Spiritualism." The *Quarterly Journal of Science* for July, 1870, contains an article under the title, "Experimental Investigation of a New Force," in which Crookes describes experiments undertaken with Mr. D. D. Home, a "medinm" well known to the public at that time. At one of the earlier *séances* the experiments were made in the presence of Dr. Huggins (afterwards Sir William Huggins, President of the Royal Society), Serjeant Cox, proprietor and conductor of the *Law Times* and *Recorder of Portsmouth*, one of Crookes's brothers, and his chemical assistant. Later, in January, 1874, the same journal published "Notes of an Enquiry into the Phenomena called Spiritual during the years 1870–73," with the signature William Crookes.

Anyone who has read these articles can realise the shock which was experienced by the scientific world on learning the character of the statements contained in them. Here was a well-known man of science, a Fellow of the Royal Society, the discoverer of thallium, with which and with its salts chemists had had time to become perfectly familiar, asserting in the most formal manner that in his presence things had been seen and done which everyone would

regard as contrary to well-established natural law and to all ordinary experience.

It is perhaps not surprising that Crookes was publicly attacked in a violent manner, but he was able to show that many misrepresentations and misstatements were made which everyone must now perceive were wholly unjustifiable. The story of his experiences as told by him is supported by evidence which would be accepted as conclusive if these statements related to any scientific work or to any ordinary occurrence. Crookes himself never withdrew or altered his statements concerning the phenomena he had witnessed, and in his Presidential Address to the meeting of the British Association at Bristol, so late as 1898, he reiterated his conviction as to their reality. This conviction he retained to the end of his life. He was President of the Society for Psychical Research in 1897. His view, if he really had a settled opinion, as to the explanation of these strange phenomena cannot be given in his own words, but the view of Mr. Serjeant Cox on the theory of what he called psychic force is given very clearly at the end of these "Notes," and it appears probable from the prominence given to this exposition that it represents very nearly the opinion of Crookes himself. Perhaps the last few lines are sufficient to quote n this place, as probably views may have changed during the forty-ive years since they were written. The passage is as follows: 'The difference between the advocates of psychic force and the Spiritualists consists in this—that we contend that there is as yet nsufficient proof of any other directing agent than the Intelligence of the Medium, and no proof whatever of the agency of the Spirits of the Dead; while the Spiritualists hold it as a faith, not lemanding further proof, that the Spirits of the Dead are the sole gents in the production of all the phenomena. Thus the controversy *resolves itself into* a pure *question of fact, only to be* letermined by a laborious and long-continued series of experiments and an extensive collection of psychological facts."

It is unnecessary to pursue the subject further, but as Crookes nade no secret of his views, and his credibility in regard to all ther questions, scientific or otherwise, has never been impugned, is biographer would not be justified in doing more or less than o place on record such statements as appear to represent fairly he position he had assumed, and certainly no biographer would be xpected to pronounce any opinion other than that which he elieves to have been entertained by the subject of his notice.

By the death of Sir William Crookes on April 4th, 1919, the orld lost a great scientific pioneer. His age was far advanced, nd the loss of his wife some three years earlier had been a severe

blow, from which he never completely recovered, so that when in January last year his friends learned of his increasing weakness, it was with the sad conviction that the end was not far off. The touching dedication prefixed to his little book on Diamonds was an indication of the domestic happiness which throughout accompanied his long and active career.

W. A. T.

THOMAS FAIRLEY.

BORN 1843; DIED FEBRUARY 21ST, 1919.

THOMAS FAIRLEY, who died on February 21st, 1919, at the age of seventy-six, had been a Fellow of the Society since 1865.

He was born in Glasgow, and received his school education in the Free Church Training College of Edinburgh, where, as is indicated by still extant evidence, he distinguished himself in classical study as well as in mathematics and physical science. He had begun to amuse himself with chemical experiments in early childhood, and his early acquired chemical taste led him, on leaving school, to become first a student with, and subsequently an assistant to, Lyon Playfair at Edinburgh University. After some time spent thus he migrated to Leeds to become a teacher in the Grammar School there and lecturer in chemistry in the local School of Medicine. At the same time he began to practice as a chemical consultant, and when the Sale of Food and Drugs Act of 1873 came into operation, he was appointed Public Analyst for Leeds and the North Riding of Yorkshire. At a later date he became official Agricultural Analyst under the Fertilisers and Feedings Stuffs Act for both the North and West Riding, having for many years previously acted as consulting chemist to the Yorkshire Agricultural Society.

He had acted both as Treasurer and as Chairman of the Yorkshire section of the Society of Chemical Industry, of which society he also became Vice-President; also as President of the Leeds Naturalists' Field Association, and as Chairman of the Leeds Institute of Science, Art, and Literature, and while holding this office he was elected Chairman of the Council of the Association of Technical Institutions of Great Britain and Ireland in 1908.

He served a full term as examiner during the earlier days of the Institute of Chemistry, and became a Vice-President of that body, in the welfare of which he always took an active and cordial

interest, and he was President of the Society of Public Analysts in 1903 and 1904.

Fairley's earliest contribution to chemical literature was a paper on "The Action of Hydrogen on Organic Polycyanides" (*Journ. Chem. Soc.*, 1864, **17**, 362). This paper incidentally records the first successful attempt at the synthesis of cyanoform, which the author prepared by heating together chloroform, potassium cyanide, and alcohol at 100° under pressure. Fairley's experiment appears to have been successfully repeated seven years later by Pfankuch (*J. pr. Chem.*, 1871, [ii], **4**, 38). Further contributions to the *Journal* were: "Analysis of Water from the 'Old Crescent Well,' Harrogate" (1875), "A New Oxide and Acid of Uranium" (1876), and "Study of Hydrogen Dioxide and of Certain Peroxides, including Experiments to determine the Heat of Formation of the Oxygen Molecule" (1877).

To the *Transactions* of the British Association he contributed papers on: "Organic Cyanides" (1865 and 1868), "The Use of Platinum Black in the Preparation of Ethylene Diamine" (1868), "Preparation of Olefiant Gas" (1868), "Preparation of Cyanogen and Hydriodate of Cyanogen" (1870), "Use of Platinised Charcoal in the Hydrogenation of Cyanogen" (1870), and "The Distillation of Sulphuric Acid" (1870).

To the *Journal of the Society of Chemical Industry* he contributed: "Note on the Detection of Certain Adulterations in Dyestuffs" (1886), "On the Estimation of Sulphur and Impurities in Coal Gas" (1886), "On the Various Forms of Filter-pumps or Water-jet Aspirators" (1887), "On the Impurities of Coal Gas" (1892), "Note on the Durabilities of Platinum–Iridium Vessels in Laboratory Use" (1896), and "The Manufacture of Ammonium Nitrate by Double Decomposition" (1897).

Published in the *Analyst* were the following papers: "Note on the Estimation of Chlorine in Water" (1893), "Arsenic Estimation relating to Malt-kilns" (1901), "Notes on the History of Distilled Spirits, especially Whisky and Brandy" (1905), and "On the Phosphates in Certain Vinegars, and the Materials used in their Manufacture" (1909). The paper on the distillation of spirits was one recording the results of interesting antiquarian research into the early antecedents of an industry which at about that time was the subject of much legal contention and of a monumental official investigation.

A paper on "The Water Supplies of Yorkshire" was contributed in 1898 to the *Journal of the Federated Institute of Brewing*.

Various other notes from Fairley's pen appeared at various times in the *Chemical News* and *Pharmaceutical Journal*, and he was

one of the contributors on subjects connected with laboratory apparatus to Thorpe's "Dictionary of Applied Chemistry."

As gas examiner to the City of Leeds, he became interested in questions relating to the manufacture and purification of coal-gas, to which he devoted a good deal of practical attention.

His health and activity were well maintained until 1911, when he had an illness from the effects of which he never completely recovered.

B. DYER.

WALTER WILLIAM FISHER.

BORN 1842; DIED FEBRUARY 7TH, 1920.

WALTER WILLIAM FISHER, Aldrichian Demonstrator in the University, Oxford, who died on February 7th, in his seventy-eighth year, had been a member of the Society since 1872.

He was educated at Worcester and Merton Colleges, Oxford, where he took a first class in chemistry in the School of Natural Science in 1870, and in the following year also succeeded in taking a class in "Greats," and he was shortly afterwards elected a Fellow of Corpus Christi College. He became chemical assistant to the late Vernon Harcourt, and in January, 1872, was appointed by the late Sir Benjamin Brodie as University Aldrichian Demonstrator in Chemistry, a post which he continued to hold until his death. For six years, from 1874, he was also lecturer in chemistry at Balliol, and he served from time to time as a public examiner for the University. He also acted as examiner to the Institute of Chemistry from 1903 to 1907, and served for several periods as a Member of Council of that body.

To the *Transactions* of the Chemical Society Fisher contributed papers on "Manganese Tetrachloride" (1878) and "Lead Tetrachloride" (1878), and to the *Proceedings* in 1892 a paper on "Anhydrous Oxalic Acid." He was a keen field botanist and a good geologist, and took a large interest in the subject of the composition of well waters from various water-bearing strata, several papers from him on this subject having appeared from time to time in the *Analyst*, notably one on "Alkaline Waters from the Chalk" (*Analyst*, 1901) and one on "Alkaline Waters from the Lower Greensand" (*Analyst*, 1902).

He had an extensive professional practice as a water analyst and as Public Analyst under the Sale of Food and Drugs Act, having been for nearly forty years Public Analyst for the counties

of Oxford, Berks, and Bucks, and also for the City of Oxford and for boroughs within the area of the aforesaid counties.

He was a man of fine physique, and in his early days was distinguished as a college oarsman, as well as on the running path; whilst during eleven years' volunteer service in the 1st Surrey Rifles in his early days he won numerous shooting prizes.

His life was lived mainly within his university, and he was less well known in the general chemical circle than were many of his contemporaries. But by those who came within the range of his genial personal friendship he was much loved and will be sadly missed.

B. DYER.

ANTOINE PAUL NICOLAS FRANCHIMONT.

BORN MAY 10TH, 1844; DIED JULY 2ND, 1919.

ANTOINE PAUL NICOLAS FRANCHIMONT, Professor of Organic Chemistry in the University of Leiden and an Honorary Foreign Member of the Chemical Society, was born at Leiden on May 10th, 1844. He came of an old French refugee family, who after 1687 migrated to Holland from the neighbourhood of Spa, where the ruins of their ancestral castle, "The Franchimont," still exist. His father was the minister of the French Church at Leiden, and had married the daughter of a Dutch pastor. The young Antoine was a weak, fragile child, too frail to be sent to school in his early years, and hence owed his primary education mainly to his father. In his later boyhood he attended the Lyceum, the principal public school of Leiden. It was intended that he should become an apothecary, and he gained his diploma in 1864, but after a few years' service he relinquished that occupation and entered the University of Leiden as a student of chemistry, obtaining his doctorate in 1871 for a thesis on "Contributions to the Knowledge of the Origin and Chemical Constitution of the so-called Turpentine Resins." His first teacher was Van der Boon Mesch, a chemist of the old school, whose contributions to experimental chemistry were almost wholly concerned with mineralogical or geochemical subjects. Organic chemistry was scarcely studied at Leiden in those days.

Accordingly, Franchimont proceeded to Bonn, where his zeal and ability were quickly recognised by Kekulé, to whom he became private assistant. He remained at Bonn about eighteen months,

and thence went to Paris to work under Wurtz. Here he gained the friendship of Friedel and Le Bel. In 1873 he returned to Holland, and was attached, as teacher of chemistry, to the school of agriculture at Wageningen, but in the following year was called to Leiden to fill the newly-created chair of organic chemistry, established on the retirement of Van der Boon Mesch, a position which he continued to occupy until his retirement on reaching the age-limit in May, 1914.

Franchimont's association with Kekulé may be said to have influenced his whole career. It had a no less marked effect on the status and development of organic chemistry in Holland. He entered on his professorship at a momentous epoch in the history of chemistry, and he was not insensible to the opportunity which the times had brought him. He came to be regarded as a missionary in the new movement which Kekulé initiated, and he made Leiden the most progressive school of modern chemistry in the Netherlands. His success may be judged from the number and variety of his published contributions to its chemical literature, and from the character of the men who were attracted by his teaching—among them may be named Lobry de Bruyn, van Romburgh, Holleman, Klobbie, van Erp, Backer, and others who have occupied teaching positions in Holland or who have associated themselves with its industrial development.

Franchimont was an excellent teacher and an admirable lecturer, enthusiastic and inspiring. His lectures were always carefully prepared according to a well-considered scheme, and he spared no effort to make them interesting and profitable. Advanced students could always learn something from his methods, from the originality of his views and the wide range of his knowledge; whilst beginners, although they might at times be perplexed by the rapidity of his utterance, and his quick-change blackboard practice, chalk in one hand and sponge in the other, could not fail to be impressed by his evident mastery of his subject.

It was, however, in the laboratory that his influence was mainly felt. He seemed to take a special interest in the work of each pupil, and regularly went his rounds twice a day. Like Kekulé, for whose methods he always expressed great admiration, he attached much importance to cleanliness and neatness of manipulation, qualities which characterised his own work. The Leiden laboratory, when he retired in 1914, showed few signs of wear, although some hundreds of students had passed through it since its opening in 1901.

His activities were, however, affected in the outset by various adverse circumstances, and it says much for his energy, persever-

ance, and patience that he should have been able to accomplish so much. During the greater part of his career at Leiden he was hampered by the conditions under which he had to work: the old laboratory was small and poorly furnished and lacked the structural fittings and appliances of modern methods of research. Holland at that period had relatively few openings for a career in chemistry, and the number of those who occupied themselves in the pursuit of that science as a profession was consequently small. Hence there was little public pressure on the Government to build and equip chemical laboratories of a type demanded by the times. As regards Leiden, the State seemed content for years to allow it to live on the traditions of Boerhaave. Franchimont must frequently have sighed for some of the arrangements he had learned to know and to appreciate in the spacious temple, which, under the inspiration and guidance of Hofmann, had been erected in the Poppelsdorfer Alleé iu Bonn. But everything comes to him who waits. After many and long delays his hopes and wishes were gratified, and, thanks to his industry and zeal, Leiden now possesses an admirably arranged laboratory for the study of organic chemistry. In its planning and equipment Franchimont took the keenest interest, sparing no trouble to make himself acquainted with every detail that would contribute to its utility and convenience. The writer recalls the lively pleasure with which he inspected the buildings of the then recently erected Government laboratories in Clement's Inn Passage, and the quick appreciation with which he noted any contrivance that wonld facilitate the operations of analytical chemistry.

When the new Leiden laboratory was opened Franchimont had occupied his chair for twenty-seven years, and much of his intellectnal vigour and creative power were spent. He used to lament that for him it had come too late, but to the last he continued to regard it with pride and affection. He could have desired no more appropriate monument by which to perpetuate the memory of his long and fruitful association with the famous old University.

On the twenty-fifth anniversary of his election to his professorship his friends presented him with his portrait, painted by the distinguished Dutch artist, Therese Schwartze, which is ultimately to pass into the possession of the University. On the occasion of the fortieth anniversary, a week before his seventieth birthday, a relief portrait in bronze by Toon Dupuis was offered to the new laboratory to be affixed to the wall of the entrance vestibule.

Franchimont, on his retirement, mainly occupied himself with his duties as one of the editors of the *Recueil des Travaux Chimiques des Pays-Bas et de la Belgique*, with which he had been

connected since 1882, and in which his own contributions to science for the most part appeared.

Although towards the end of his days his physical strength was greatly impaired, and he suffered acutely at times from the effects of the painful malady to which he ultimately succumbed, his mind continued active and alert to the last, and he read and corrected proof-sheets to within a week of his death on July 2nd, 1919.

A man of simple tastes and habits, happy in his relations with his colleagues and pupils, and in his home life—he had married Miss Cornelia van Batenburg, a member of an old Gelderland family, in 1880—his interests were wholly centred in the duties and responsibilities of his office. He lived the serene, contemplative existence of the philosophic student, devoting his life to the elucidation of a special class of phenomena. The character of his studies was, of course, mainly determined by the requirements of his professorship, but his knowledge as a chemist was by no means limited to his own department. He was an omnivorous reader, and followed the development of every section with equal interest. He had a sound judgment, a strong logical faculty, and keen intuitive power—qualities which made him an admirable editor and a capable and judicious critic. He was blessed with a happy temperament and a genial manner, and had the saving grace of humour. Although absorbed in his work, and apt to resent interruptions to it by the routine calls of academic trivialities, he was in no sense a recluse, but when the occasion demanded took his full share in the management of university affairs.

Franchimont's first published paper on "Turpentine Resins" appeared in the *Archives Néerlandaises* for 1871, and was quickly followed by communications on heptylic acid and heptyl alcohol. With Kekulé he discovered triphenylamine, and he detected the formation of anthraquinone in the preparation of benzophenone. These, it is believed, were the only papers on aromatic chemistry with which he was directly concerned. During his stay in Bonn he also worked with Zincke on the aliphatic derivatives from Heracleum oil—a subject which had already engaged his attention before his visit to Germany. Indeed, he seemed almost exclusively attracted to the chemistry of aliphatic compounds, and practically the greater part of his memoirs, as well as those he published in collaboration with his pupils, deal with this class of substances. During the forty years of his activity at Leiden upwards of one hundred contributions to the periodical literature of chemistry emanated from his laboratory, apart from the many graduation theses which he may have inspired. Considerations of space prevent any detailed examination of this mass of work, but certain

papers of special significance require notice. Among them is the memoir on the "Acetylisation of Glucose" (1879), leading to the isolation of the penta-acetate, which subsequently played so important a part in Emil Fischer's researches on the isomeric derivatives of glucose. Next is the paper on the "Acetylisation of Cellulose" (1879–1881), when he prepared three acetates, one of which was afterwards identified by Skraup and König, in 1901, as the octa-acetate of cellobiose. From these researches originated the methods of acetylation now in common use, thereby laying the foundations of an important technical industry.

Franchimont's name is, however, principally associated with the study of the nitroamino-compounds—a class of substances with which the Leiden laboratory is identified. In collaboration with van Romburgh he investigated the action of nitric acid on dimethylaniline, which resulted in the discovery of trinitrophenylmethylnitroamine—the "tetryl" of these later days. Franchimont also prepared dinitrodimethyloxamide and dimethylnitroamine.

With Klobbie (1888) he obtained methylnitroamine, an acid substance isomeric with Frankland's dinitromethylic acid, by the action of ammonia on methyl nitrourethane.

With his pupil, van Erp, he found (1894) that alkylation of the monoalkylnitroamines gives not only the dialkylnitroamines, but also isomeric forms, which may be regarded as oxygen esters—one of the first of the illustrations of isomerism to be studied by Hantzsch with his theory of pseudo-acids.

A complete list of Franchimont's papers, together with the titles of the various graduation theses which originated in his laboratory, has been compiled by his pupil, Professor Backer, and is published in the *Chemisch Weekblad*, 1914, No. 18.

Franchimont was also the author of several text-books on organic chemistry which had a considerable measure of popularity in their day, but have now been largely superseded by more modern works. Compilation of literature of this kind was not a congenial task to a mind of his originality.

Franchimont was an Officer of the Order of the Dutch Lion, and of the Légion of Honour, and a member of the Dutch Academy of Sciences of Amsterdam. He was elected an Honorary Foreign Member of the Chemical Society in January, 1898.

My acknowledgments and thanks are due to Miss J. J. P. Brants, a niece of the late Professor Franchimont, and also to Professor Backer, of the University of Groningen, for the information and assistance they have afforded me in the preparation of this notice.

T. E. THORPE.

HAROLD CECIL GREENWOOD.

Born May 3rd, 1887; Died November 4th, 1919.

Harold Cecil Greenwood, O.B.E., D.Sc., F.I.C., was born at Edenfield, near Manchester, on May 3rd, 1887, and was educated at the Grammar School, Bury. He entered for his Science Course at Manchester University at an early age, and graduated as B.Sc. with first-class honours in chemistry in 1907. He obtained in succession the Mercer Scholarship, the Beyer Fellowship, and an 1851 Exhibition Scholarship. During this period the Electrochemical Department of the University was constituted under Dr. R. S. Hutton, and Greenwood became one of his most enthusiastic students. He carried out a series of important researches on the production of ferro-alloys, the reduction of refractory oxides, and on the boiling points of metals, first at atmospheric pressure, afterwards studying the effect of reduction of pressure on the boiling point. Later he employed some of the pressure furnaces designed by Dr. J. E. Petavel for further study under increased pressure. His researches in this field furnish the accepted data for most of the substances he studied. On obtaining the 1851 Scholarship, Greenwood proceeded to Karlsruhe, where he worked for a period with Professor Haber. Following up the earlier work of Haber and Le Rossignol, Greenwood's research on the synthetic production of ammonia by means of the uranium carbide catalyst, and his study of the details of this reaction under varying conditions of flow rate, temperature, pressure, etc., probably marked the stage at which it was first realised that a successful technical process might be founded on it. The Badische Company had already begun to take an interest in the developments at Karlsruhe and to help to finance the expenses of the research; therefore when, after six months' work, the time arrived for a report of progress to be furnished by Greenwood to the Commissioners of the 1851 Exhibition, he was obliged to go before some of the Badische directors to be catechised as to what use would be made in England of the report. Would it fall into the hands of Sir William Ramsay? The publication of this research, and of a number of others carried out by Haber's co-workers at Karlsruhe about the same period, was held over until after the outbreak of war, by which time the technical success of the synthetic ammonia process had been assured.

Greenwood returned to England in the year 1910, and worked for some time in the Heat Division of the National Physical

Laboratory on the specific heat of metals at high temperatures, elaborating the method formerly employed by Harker in his determination of the specific heat of iron. He obtained the D.Sc. from Manchester University in 1912, and became a Fellow of the Chemical Society in the same year. He was subsequently appointed Research Chemist to the firm of William Hutton and Sons, Ltd., of Sheffield, where he investigated problems cognate to the electroplating industry.

Early in 1916, when the submarine campaign had begun to cause anxiety as to the country's supplies of sodium nitrate from Chile, the Faraday Society appointed a small committee to prepare a memorandum on the question of nitrogen fixation for submission to the Ministry of Munitions. Of this committee Greenwood subsequently became a member. After a number of preliminary conferences, the Nitrogen Products Committee of the Ministry was constituted, and among its other activities it was decided to commence experimental work on certain problems relating to fixation. Although at that time it was not anticipated that there would be any shortage of supplies of ammonia, yet it was deemed desirable, in view of the suitability of the synthetic ammonia process for the needs of the country, that an experimental study of it should be made forthwith, so that the required information should be available if necessary. Greenwood at the time was serving as a technical officer in the R.N.V.R., but in view of his previous experience his services were requisitioned at the writer's suggestion, and he became the head of the Synthetic Ammonia Section of the Research Laboratory established by the Munitions Inventions Department. This was located in premises placed at the disposal of the Government in the new Ramsay building at University College, chiefly through the instrumentality of the Provost and Professor Donnan. In the early stages of the work there were many difficulties with which to contend, but in his section a considerable measure of success was quickly achieved by Greenwood and his collaborators. After a year's experimentation, it was decided by the committee to establish a technical plant on a moderate scale, since by means of this plant it was hoped that a study of the chemical engineering problems could follow on that already made of the pure chemistry of the reactions involved.

Early in 1918, however, the engineers of the Explosives Department decided that the progress made justified them in proceeding with a scheme for the erection of a large works for the manufacture of synthetic ammonium nitrate, and a site on the River Tees was ultimately chosen, and building operations were begun. At the time of the Armistice, however, the factory was far from

complete, and since then arrangements have been made for its transfer from Government ownership to private enterprise. In the following autumn Greenwood was taken over into the service of the Syndicate which was to assume control of the new development. He had been engaged only a few weeks on his new duties as their chief research chemist when he was suddenly taken ill. After a few days' illness he died from blood poisoning at Winnington Hall, Northwich, on November 4th, 1919, at the early age of thirty-two years.

Dr. Greenwood married, in 1913, Miss M. G. Horsfall, who, herself a graduate in science, was able to render her husband valuable assistance in his work. He leaves no family.

Just before his death he had completed for press an important work on "Industrial Gases" for Dr. Samuel Rideal's series, which has since been published.

Although of a rather shy and retiring disposition, the reverse of dogmatic, and not excelling as an expositor, Greenwood possessed the true research instinct, and had a genial and attractive personality. He won the esteem of all who worked with him. His output of research was one of which many a much older man would have been proud; by his death, experimental applied chemistry suffers a severe loss.

J. A. HARKER.

CHARLES EDWARD GROVES.

BORN MARCH 4TH, 1841; DIED FEBRUARY 1ST, 1920.

THOUGH during the last twenty years of his life the figure of C. E. Groves was less familiar than formerly to the Fellows of the Chemical Society, no one was better known and esteemed during the long period in which he held office as Editor of the *Journal*.

Groves was born at Highgate on March 4th, 1841, but while still a young child his parents removed to Kennington, and in that neighbourhood he remained until the end of his life. He was educated at Brixton College School, and subsequently entered the Royal College of Chemistry under Hofmann, the first professor. In October, 1862, he became chief private assistant to Dr. John Stenhouse, F.R.S., who had a laboratory for research in Rodney Street, Pentonville. This was an almost unique establishment. Stenhouse had been for some years lecturer on chemistry at St. Bartholomew's Medical School, but about the year 1856 he had

been disabled by a paralytic stroke, from which he partly, but never wholly, recovered. His interest in chemical investigation prompted him, notwithstanding his crippled condition, to resume his researches into the nature of the crystalline constituents of lichens and other vegetable materials, and he found premises to suit his purpose in an old house to which was attached the outbuildings of an abandoned artificial flower factory. Here early in 1860 he established himself with E. J. Mills (afterwards professor in Glasgow) as his scientific assistant. Mills was succeeded in Stenhouse's laboratory by C. E. Groves, together with W. A. Tilden as junior. When the latter left, for a post at the Pharmaceutical Society, he was succeeded by R. Meldola (afterwards President of the Chemical Society) and T. Bolas. The little laboratory was always busy, and Groves remained in command until the death of Stenhouse in 1880. During the later years of this association the papers resulting from the work done were published in the joint names of Stenhouse and Groves. Both were men of earnest religious convictions, and "the Doctor," who could only sit and watch operations, was much disposed to talk during work, which was not unfrequently interrupted by controversy on subjects connected with their respective religious views, Stenhouse being a Presbyterian and great admirer of the famous preacher Charles Spurgeon, while Groves, as a high churchman, stood up for the episcopal establishment.

In 1865 Stenhouse succeeded Hofmann as one of the external Assayers to the Royal Mint, and held the office until it was abolished by Mr. Robert Lowe in 1870. Stenhouse, of course, was incapable of any sort of manipulation, and the work was done by Groves with the aid of a technical assistant.

In 1877, when the Institute of Chemistry was founded, Groves took an active part in the movement and was appointed Secretary; from 1887 to 1892 he was also Registrar. He was connected with the *Journal of the Chemical Society* from 1878, first as Sub-Editor and in 1884 as Editor, in succession to Mr. Henry Watts. This office he resigned in 1899. Soon after Dr. Stenhouse's death in 1880 Groves was appointed Lecturer on Chemistry and Dental Metallurgy in the Medical School at Guy's Hospital, retiring in 1901. For more than twenty years he was also consulting chemist to the Thames Conservancy Board, and gave up this work in 1909. For only a few years later he was able to sustain his interest in scientific work, but failing health compelled him to retire from active life or study, and he died at his house on Kennington Green, February 1st, 1920.

Groves became a Fellow of the Royal Society in 1883.

Groves was a good manipulator and skilful analyst. His familiarity with several languages and his extensive knowledge of physical and chemical science were valuable qualifications for the post of Editor, though he may perhaps be remembered for certain peculiarities of phraseology in English on which he insisted and which sometimes brought him into conflict with less scrupulous contributors to the pages of the *Journal*.

In early life he was a great walker, and though in frame very spare he was both muscular and active. Though not addicted to games, he found his recreation in monntaineering, and for many years his summer vacations were spent in Switzerland. He will be remembered by many among the older members of the Alpine Club.

W. A. T.

JOHN HOLMES.

BORN JANUARY 15TH, 1871; DIED OCTOBER 1ST, 1919.

JOHN HOLMES, who died on October 1st, 1919, after a short illness, at the age of forty-eight, received his early education at Giggleswick School. Entering the Royal College of Science as a revenue student in 1894, he passed with much credit through the prescribed course of studies, and was afterwards employed in the Government Laboratory—first as a chemical assistant, and subsequently as a member of the permanent analytical staff. During the early part of this period he carried out several investigations in collaboration with Sir Edward Thorpe, including one on the occurrence of paraffins in the leaf of tobacco (T., 1901, **79**, 982), and one on the constitution of the fat present in the yolk of eggs. Later, he worked out the now well-known "Thorpe and Holmes" method for the quantitative estimation of methyl alcohol in mixture with ethyl alcohol by oxidation of the former to carbon dioxide. Much of his work at this period was concerned with questions relating to alcohol, and in the laborious task of compiling a series of revised alcoholometric tables, published officially in 1912, Holmes had a prominent part. A process for the accurate determination of ethyl alcohol in commercial fusel oil is also due to him.

Problems in physical chemistry, especially those concerned with the theory of solutions and the intermiscibility of liquids, had always a great interest for Holmes. A series of papers by him on these subjects has appeared in the Society's *Transactions* (1907, 1908, 1909, 1913, 1915, and 1918). Although lucid exposition was

not the author's *forte*, the experimental results disclosed in some of these papers are quite noteworthy; and it might, perhaps, well repay some physical chemist, who is not too much trammelled by accepted theories, to look carefully into these researches, even if it should turn out that he is not in agreement with the author's theoretical explanations of the results obtained.

Holmes was a man of equable temper and kindly disposition. In his younger days he was an excellent all-round man at sports, and could point with pardonable pride to a goodly collection of trophies carried off in athletic contests. Scientifically, his bent was distinctly that of the investigator. He was never so happy as when, the day's work done, he could devote his spare hours to following up in the laboratory some new clue revealed by previous experiments, or some fresh line of thought which his reading had suggested. In his modest way he was veritably of those "who seek knowledge simply because they crave for it"; and to a Fellow of the Chemical Society no better tribute than this can be paid.

C. SIMMONDS.

SIR BOVERTON REDWOOD, BART.

BORN APRIL 26TH, 1846; DIED JUNE 4TH, 1919.

SIR BOVERTON REDWOOD, who died on June 4th, 1919, after a brief illness, was the eldest son of Dr. Theophilus Redwood, of Boverton, Glamorganshire, who was for forty years Professor of Pharmacy in the Pharmaceutical Society at Bloomsbury Square. It was quite natural, therefore, that Boverton Redwood chose the study of chemistry as a profession.

Boverton Redwood was born near to the scene of his father's activities at 19 Montague Street, Russell Square, on April 26th, 1846. He studied at University College School, where he showed his inclination for the pursuit of science. On leaving University College he entered his father's laboratory, where he received his early instructions in practical chemistry. In 1866, at the age of twenty, he was elected a Fellow of the Chemical Society and twice served on the Council.

In 1869 he was appointed Secretary and Chemist to the Petroleum Association, and this caused him to turn his attention to the study of mineral oils, a subject at that time quite in its infancy, the chemical side of which had scarcely been touched. In fact, the American oil had only recently been struck, and at that

time the chief source of mineral oil was the distillation of shale by Young's process. In a short time he became the leading expert on the subject of mineral oils, and kept pace with its rapid developments until the day of his death.

His earliest recorded work in connexion with mineral oils had to deal with the testing of the flash point. In 1872 he gave evidence before a select committee of the House of Lords on the subject, and in 1877, in conjunction with Sir Frederick Abel, he carried out researches which resulted in standardising the methods of testing for flash points and the establishment of the Abel apparatus as the legal basis for testing flash points of low flash oils. In the same year he visited the United States to carry out further investigations on the subject.

In 1881 he studied the effect of barometric pressure on the gaseous constituents dissolved in oils. These tests were carried out at various heights in the Alps and in a pressure chamber at Berlin. Following up this line of investigation he visited India and carried out further tests as to the influence of climate. As a result of this work he—jointly with Sir Frederick Abel and Dr. Kellner—advised the Government of India in amending the Petroleum Act.

He travelled considerably and examined petroleum wells in all parts of the world, and by this means obtained a first-hand knowledge of the oil industry and followed its developments.

In 1886 he turned his attention to the viscosity of lubricating oils, and designed the Redwood viscosimeter, which has become the standard instrument in the British oil industry. Recently he devised a modified form for use with heavy fuel oils, and this is now known as the Admiralty standard.

In 1892 Redwood visited Egypt in reference to the transport of oil in bulk through the Suez Canal. In 1894 the Institution of Civil Engineers awarded him the Telford premium for his work in reference to the accumulation of petroleum vapour in tanks and difficultly accessible parts of ships carrying petroleum. He designed a special apparatus for testing for the presence of such vapours. About the same time, in conjunction with his brother, Robert Redwood, and Mr. H. Barringer, he invented the Redwood water-finder, an instrument for determining the amount of water which has collected beneath the oil in tanks.

Redwood was one of the first to attempt the cracking of oils for the production of lighter oils from heavy residues. In this connexion he and Sir James Dewar patented a process in 1889 for distilling and condensing oils under high pressure. This resulted in the heavier grades of oil yielding lighter oils and spirit. At

this time, however, there was not much call for light oils, and the process was not worked on a large scale.

As might be expected from his interest in oils for fuel and other purposes, he early took an interest in motor-cars, and more than twenty years ago the first four-cylinder Daimler car was constructed to his order and was exhibited to King Edward VII. (then Prince of Wales).

Besides his interest in his life-work, Redwood took very active interest in international exhibitions, and acted as chairman to the chemical section of the Royal Commissions for the Exhibitions of Brussels and Turin. He also served on the Committees of the Rome and St. Louis Exhibitions. He was a man of great activity and extreme conscientiousness, and beside looking after his business and advising his clients, served on committees of scientific societies, from which, when a member, he was rarely absent. It was, in fact, difficult to realise how he concentrated so much work within the working day.

During the war he served as Assistant Controller in the Trench Warfare Research. He was also Director of the Petroleum Research Department, and in this connexion supervised a large number of tests on the carbonisation of coals and other bituminous materials with the object of obtaining oils, so that this country might be self-contained and not require to procure the oils from abroad. Later he was appointed Director of Technical Investigations to the Petroleum Executive.

In 1913, at his instigation, the Institute of Petroleum Technologists was founded, and he was elected its first President.

Redwood was knighted in 1905 and received a baronetcy in 1911. The title passes to his grandson, Thomas Boverton Redwood.

Sir Boverton was adviser on petroleum to the Admiralty and Home Office, the India Office and the Colonial Office. He also acted as consulting adviser to the Corporation of London under the Petroleum Acts, and adviser to the Thames Conservancy. His treatise on petroleum, first published in 1896, is the standard English work on the subject. He wrote another work on petroleum in 1901 in conjunction with Captain J. H. Thomson, and published a number of papers on the subject before different industrial scientific societies.

As a man, Redwood had a most charming manner with an old-world courtesy. He was always willing to help the younger generation, and would take an infinite amount of trouble to help young men commencing their career. He was a staunch friend, and never spoke unkindly even of those with whom he did not agree. He had a habit when he met his friends of putting his

hands on their shoulders and saying, "Well, friend, and how are you to-day?" Those who knew Sir Boverton Redwood felt a very personal loss of a kind friend and counsellor. He died in harness, and only a few days before his death was enthusiastically examining the first oil struck in this country.

F. MOLLWO PERKIN.

JOHN CHARLES UMNEY.

BORN MARCH 13TH, 1868; DIED OCTOBER 9TH, 1919.

J. C. UMNEY was a pharmacist of a type that is none too common. He declared that he loved pharmacy, and was proud of being a pharmacist.

His father, Charles Umney, was a Fellow of the Chemical Society from 1865 until the time of his death in 1916, and an original Fellow of the Institute of Chemistry. He did pioneer work in bringing trained technical knowledge into the wholesale drug trade, and became one of the most prominent wholesale druggists of his day.

John Umney may thus be said to have been born into the drug trade. He was educated at Dulwich College, where he gained a scholarship, and at the Pharmaceutical Society's School of Pharmacy, where he was a medallist. After passing his examinations he worked in the Pharmaceutical Society's research laboratory under Professor Dunstan, with whom he was joint author of a paper on aconitine, which was published in the *Transactions* in 1892. He was elected a Fellow of the Society in the following year.

His first publication, made in 1889, was a note on the analytical characters of oil of anise. Thus did he early identify himself with essential oils, in connexion with which he is so well remembered. The literature of many essential oils has been enriched through his work, which consisted largely in the examination of new oils, of known oils from new sources, and occasionally of exposures of new and scientific methods of adulteration. Among others, he worked on the oils of anise, bergamot, cajuput, cloves, cinnamon, citronella, dill, eucalyptus, fennel, juniper, lavender, lemon, lemongrass, neroli, peppermint, pine, and rose, and his papers on the essential oils alone number upwards of fifty.

In 1912 the Fairchild Memorial Lectures delivered before the Pharmaceutical Society took the form of a short course of lectures on the terpenes and essential oils. The first of these, on "The History and Chemical Relations of the Terpenes," was delivered by Sir William Tilden; the second, on "The Synthesis of the Terpenes," by Professor W. H. Perkin. J. C. Umney was selected to give the third and fourth lectures, the title of which was "Essential Oils, their Constitution and Commerce."

Umney was a member of the Committee of Reference in Pharmacy concerned in the preparation of the 1914 edition of the British Pharmacopœia, and was part-author of the paper on "The Essential Oils of the British Pharmacopœia," which was read before the Pharmaceutical Society and formed the basis of the monographs now official in that book. He also contributed the article on "Essential Oils" in Thorpe's Dictionary of Applied Chemistry.

Umney published papers on fixed oils also, particularly almond, olive, cod liver, and fish liver oils, and many dealing with crude vegetable drugs, making valuable suggestions as to standards for these and other medicines.

His original contributions to pharmaceutical literature during a quarter of a century cover a wide range of subjects. In addition to scientific papers, and articles of a technical and commercial nature, he made valuable communications on subjects usually comprehended in the term "Pharmaceutical Politics." His publications were made chiefly in the *Pharmaceutical Journal*, and at the annual meetings of the British Pharmaceutical Conference. Latterly his communications appeared in *The Perfumery and Essential Oil Record*, which journal he himself founded and edited with conspicuous success.

At an unusually early age, in fact while still a student, John Umney began to exhibit signs of remarkable business capacity, and perhaps the most striking characteristic in his outstanding personality was his great executive ability.

Upon leaving the Pharmaceutical Society's research laboratory he entered his father's firm of wholesale druggists, and remained a director up to the time of his death. Sacrificing to some extent original work on the scientific side for the organising and more purely commercial aspects of pharmacy, John Umney rapidly reached a prominent position in the drug trade, and while still comparatively young was possibly the best known man in the world of pharmacy.

During the course of his business career he filled many offices, and in particular was President of the British Pharmaceutical Conference (1912–1913), President of the Drug Club (1908–1911),

$\frac{Vr(s-\sigma)}{\eta}$ is small (see Edser, "General Physics," p. 489, or Poynting and Thomson, "Properties of Matter," p. 222).

Stokes's equation applies only to a sphere falling through an infinite extent of liquid, but the velocity of a small sphere falling axially through a viscous liquid in a cylinder has been discussed mathematically by Ladenburg (*Ann. Physik*, 1907, [iv], **23**, 9 447), Lord Rayleigh (*Phil. Mag.*, 1893, [v], **36**, 354), and Allen (*ibid.*, 1900, [v], **50**, 323), and Ladenburg (*Ann. Physik*, 1907, [iv] **22**, 287) made use of the principle for the determination of the viscosity of Venice turpentine under pressure. Sheppard (*J. Ind. Eng. Chem.*, 1917, **9**, 523) has used the method of the falling sphere for the determination of the absolute viscosity of viscous liquids, such as solutions of nitrocellulose, but the correction formula for the effect of the walls of the vessel on the time of fall of the ball applied by him is not that reached mathematically by Ladenburg, Rayleigh, and Allen, which we have found to be correct experimentally. Further, the comparatively large-sized balls used by Sheppard are not an advantage.

According to Ladenburg, there are two linear corrections to be applied to the simple Stokes' equation for the case of a small sphere falling axially through a viscous liquid in a cylindrical tube, a correction for wall-effect and one for end-effect.

The correction for wall-effect is

$$V(1 + 2{\cdot}4\,x) = V_{\infty} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x is the ratio of the radius of the sphere to that of the cylinder, V is the velocity of the sphere, and V_{∞} the velocity of the sphere corrected for an infinite medium. This formula was confirmed experimentally for tubes and balls of the radii used by us, but fails when x becomes large, hence for a steel ball of given diameter the diameter of the tube employed must be sufficiently large for the correction to apply. Sheppard used for a correction the empirical formula $T = T_{\infty} + \frac{c}{(r-1)^n}$, where T is the time of fall of the sphere through a length s, T_{∞} the time of fall in an infinite medium, r the ratio of the radius of the cylinder to that of the sphere, c a constant depending on the diameter of the sphere, and n is a constant taken by Sheppard as 2.

From the form of this expression, it is an endeavour to apply a correction for cases when the diameter of the tube is not large enough relatively to the sphere for the linear correction of Ladenburg to apply, but although the expression may fit the author's

ata when suitable constants are chosen, this does not prove that he value of T_∞ obtained is the correct one.

The correction for end-effect has not been taken into consideration by Sheppard. It is of less importance than that for wall-effect, but is appreciable. If the velocity is measured in the middle third of the tube, the correction is

$$V_\infty = \left(1 + 3{\cdot}3\,\frac{r}{h}\right)V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where r is the radius of the sphere and h is the height of the liquid.

The complete equation, including both corrections, for the falling sphere viscosimeter is consequently

$$9\eta V(1 + 2{\cdot}4\,x)\left(1 + 3{\cdot}3\,\frac{r}{h}\right) = 2\,gr^2(s - \sigma) \quad . \quad . \quad . \quad (4)$$

or, if the time of fall T through a length s is measured,

$$9\eta s(1 + 2{\cdot}4\,x)\left(1 + 3{\cdot}3\,\frac{r}{h}\right) = 2\,gr^2(s - \sigma)T \,. \quad . \quad . \quad . \quad (5)$$

If spheres of equal radius are used in tubes of the same dimensions, the only variables are relative density, viscosity of the liquid, and time of fall. A simple equation,

$$\frac{\eta}{\eta_1} = \frac{(s - \sigma)T}{(s - \sigma_1)T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

resembling the expression used for the Ostwald pattern of capillary viscosimeter, can then be employed to obtain the viscosity of a liquid when the time of fall for another liquid of known viscosity is known. This permits of the standardisation of viscosimeter tubes by means of a standard liquid the viscosity of which has been determined, either in a tube, the dimensions of which have been accurately measured, or by another method.

Selection of Components.

The considerations which influenced the specification of the apparatus may now be discussed.

In the choice of a sphere, uniformity of diameter is most important, and steel ball-bearings are very satisfactory in this respect. They are guaranteed by the makers to be correct within 0·0025 mm. Tested by the measurement of one gross of balls, this was found to be the case. The possible error on the radius of the sphere when a ball of 0·15 cm. in diameter is taken is therefore only 0·16 per cent.

A ball of 0·15 cm. in diameter was chosen as the standard size, as it was the smallest stock size. The advantages of using the smallest ball available are that the correction factors may be applied to tubes of small diameter, and since the expression $\frac{Vr(s-\sigma)}{\eta}$, which must be small for Stokes's equation to hold, decreases with r, that valid results may be obtained over a wider range of liquids. The density of the steel of which the ball bearings are composed was determined for one gross of balls, and found to be 7·65.

It is unlikely that great variations exist in the density of ball-bearings, and error can always be avoided by determining the density of the balls in use.

Before the standard diameter for the viscosimeter tube was fixed, many experiments were made in which a sample of castor oil was used as the liquid, and the times of fall of standard 0·15 cm spheres in tubes of different diameters were determined.

The results obtained at 20° with five tubes are given in table I.

TABLE I.

Diameter of tube. Cm.	Time of fall for 15 cm. Seconds.	x.	Time of fall, infinite medium. Seconds.
0·85	25·2	0·187	17·4
1·14	21·8	0·1395	16·3
2·10	18·8	0·0757	15·9
3·50	17·7	0·0454	15·95
4·54	17·4	0·0350	16·0

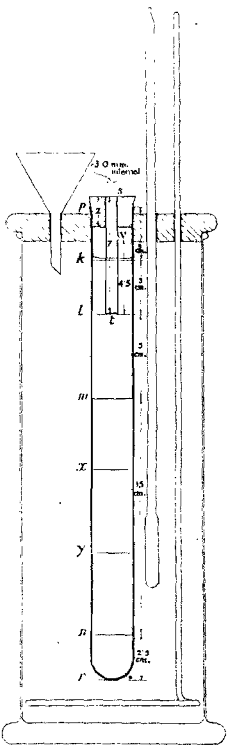
It will be seen that the time of fall, calculated for an infinite medium, becomes constant for the wider tubes. The small differences are ascribed to irregularities in the bore of the tubes.

For the standard tube, an internal diameter of 2±0·05 cm was specified as coming within the limit of applicability of the correction factor, whilst being more convenient than wider tubes. The maximum error involved in taking these tubes as exactly 2 cm. in diameter without measurement is 0·4 per cent., since the correction factor for 1·95 cm. is 1·195, for 2 cm. 1·1905, and for 2·05 cm. 1·186. In technical work, an error of this magnitude may often be neglected, but it is preferable to standardise each tube by measuring the time of fall with a liquid of known viscosity for accurate work. If the values of η_1, σ_1, and T_1 for the liquid of known viscosity and s the density of the steel are substituted in equation (6), it becomes

$$\eta = K\,(s-\sigma)T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where K is a numerical constant involving all the corrections for the particular tube, termed the tube constant.

The total length of the viscosimeter tube was fixed at 29 cm., and it was divided into three 5-cm. lengths for measurement of time of fall, another 5 cm. was allowed for the ball to acquire its uniform velocity, and a further graduation mark fixed the height of the liquid in the tube. To deliver the sphere into the centre of the tube, the following simple device was found satisfactory. The tube was closed by an india-rubber stopper, bored centrally, with a glass tube of 3 mm. internal diameter and 7 cm. long passing through it.



This tube was adjusted to dip 3 cm. below the surface of the liquid in the viscosimeter tube, a small hole in the side wall of the releasing tube just below the stopper serving to adjust the pressure inside and outside the tube. The sphere, when dropped into the releasing tube, travels very slowly down it, and is freed from air bubbles; it then leaves the end below the surface of the liquid with the minimum of disturbance and in the centre of the tube.

The accompanying diagram shows the arrangement of the apparatus.

Viscosity of Castor Oil.—Castor oil was chosen as a convenient standard liquid.

The viscosity of castor oil has been determined over a range of temperature by Kahlbaum and Raber (*Kais. Leop-Carol. Deut. Akad. Naturf. Halle*, 1905, **84**, 203).

Table II gives a few of their results.

TABLE II.

Temperature.	16·1°	19·6°	22·6°	24·8°	26·4°
Viscosity in C.G.S. units	13·704	10·272	7·908	6·592	6·003

The viscosity at 20° is therefore 9·9.

The time of fall of a standard ball through 15 cm. of castor oil in a standard viscosimeter tube of 1 cm. radius at 20° was found to be 19·4 seconds.

Substituting in equation (5), this gave

$$9 \times \eta \times 15 \times 1{\cdot}1905 \times 1{\cdot}0103 = 2 \times 981 \times 0{\cdot}0794^2 \times 6{\cdot}69\,;$$

hence $\eta = 9{\cdot}888$.

The density of the castor oil was 0·96 and the density of the steel 7·65.

The result obtained with the falling sphere viscosimeter is remarkably close to that obtained by Kahlbaum and Raber, and indicates that the instrument may be used with confidence to determine the viscosity of liquids with similar or greater viscosity.

Summary.

The theory of the falling sphere viscosimeter is briefly discussed and the magnitude of some corrections and errors are indicated.

The bearing of these on the design of an instrument for general use is discussed.

The viscosity of castor oil determined by this instrument is shown to agree with the valne found by Kahlbaum and Raber.

This work was carried out at the Research Department, Royal Arsenal, Woolwich, and is published by permission of the Director of Artillery, War Office, to whom our thanks are due.

We also desire to express our thanks to Lieut.-Colonel R. A. Craig, C.M.G., and to Sir Robert Robertson, K.B.E., F.R.S., for the interest they have taken in this work.

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LII.—*The Viscosity of Solutions of Cellulose.*

By WILLIAM HOWIESON GIBSON.

PART I.

DURING the progress of work in connexion with the manufacture of propellant powders, some observations of general interest on the viscosity of solutions of cellulose have been made, and this paper gives a brief account of this portion of the work.

Very many determinations of viscosity have been made, so a selection only has been given.

A number of determinations of the viscosity of cuprammonium solutions of various forms of cellulose, such as cotton, wood-pulp, etc., were made by Ost (*Zeitsch. angew. Chem.*, 1911, **24**, 1892), who claimed that viscosity determinations carried out by his method gave useful information on the nature and technical value of celluloses.

As the determination of viscosity seemed to be a promising method of obtaining information of technical value, a considerable number of experiments were carried out by Ost's method, but the results were far from satisfactory, owing to the progressive changes which took place in the solution, which are referred to in Ost's paper.

In order to improve the method, elimination of the progressive change in the solutions was essential, and as air-oxidation seemed a probable cause, complete exclusion of air was tried.

The difficulties in obtaining trustworthy viscosity determinations were overcome in this way by the use of the hydrogen capillary viscosimeter, and, later, the falling sphere viscosimeter (see Part II).

Although the hydrogen capillary viscosimeter was somewhat troublesome to manipulate and could only be used for solutions of cellulose up to 1 per cent., it was found very useful in studying the effect of various treatments on cellulose.

The viscosity in C.G.S. units of 1 per cent. solutions in cuprammonium of twenty-eight samples of purified cotton-waste examined in the hydrogen capillary viscosimeter ranged from 4·53 to 0·14, and the viscosity of a trade sample of unpurified waste was found to be 7 units. These results indicated that considerable difference existed between different samples of purified cotton-waste, which could probably be ascribed to difference in treat-

ment. The high viscosity of unpurified cotton was also definitely established.

The effect of variation in the conditions of treatment of cellulose with sodium hydroxide solutions on the viscosity of the product was studied on the laboratory scale, using the hydrogen capillar viscosimeter.

The results obtained in these experiments are given in th following tables, and are plotted in Fig. 1.

TABLE I.

Conditions of boiling. Cotton 100 parts. NaOH 18 parts.	Number of curve in Fig. 1.	Viscosity in 1 per cent. solution C.G.S. units. Time of boiling in hours. 0.	1½.	3.	6.	9.	12.
Pressure, 5·6 kilos. per sq. cm.							
4 per cent. NaOH solution.	I.	14·48	0·40	0·13	0·09		
2 ,, ,, ,,	II.	14·48	0·54	0·21	0·14		
Pressure, 2·8 kilos. per sq. cm.							
4 per cent. NaOH solution.	III.	14·48	2·51	1·46	0·84	0·45	0·42
2 ,, ,, ,,	IV.	14·48	3·61	2·40	1·87	0·75	0·5[illegible]
Pressure, 1·4 kilos. per sq. cm.							
4 per cent. NaOH solution.	V.	14·48				2·65	
2 ,, ,, ,,	VI.	14·48				3·90	

TABLE II.

		Parts of NaOH solution to 1 part of cotton. 2.	4.	8.	16.
Pressure, 5·6 kilos. per sq. cm. Time 1½ hours.					
4 per cent. NaOH solution	....	0·43	0·40	0·29	0·32
2 ,, ,, ,,	....	1·27	0·72	0·54	0·53

Consideration of these results leads to the following conclusions

(1) Temperature is the main factor in reducing the viscosity of cotton during boiling with sodium hydroxide.

(2) The viscosity falls rapidly at the beginning of the exper ment, and the rate of fall slackens as the boiling continues.

(3) The concentration of sodium hydroxide solution influence the viscosity. With a 2 per cent. solution, the viscosity

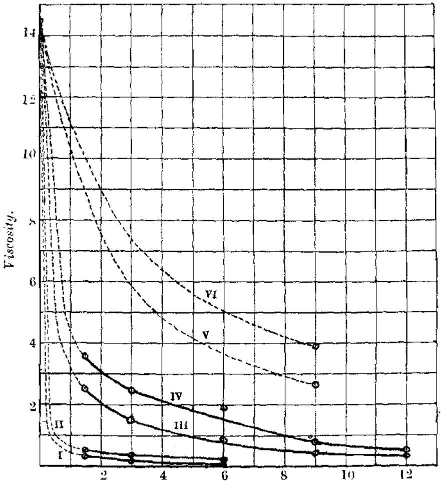
approximately about 50 per cent. higher than with a 4 per cent. solution.

(4) At high temperatures, the viscosity falls so rapidly that the *concentration* of the solution is of little practical importance.

(5) With *mild treatments*, the actual difference between concentrated and dilute solutions is more pronounced.

(6) When the proportion of solution to cotton is increased, the

FIG. 1.



Time of boiling in hours.

viscosity is reduced. This may be due to the concentration of the solution remaining more uniform during the boiling.

The experiments indicated quite clearly that the viscosity of purified cotton could be coutrolled by controlling the conditions of the boiling process. Examination of samples of bleached and unbleached cotton-waste were made, and led to the conclusion that the process of bleaching with weak bleaching powder solution

had little effect on viscosity. The effect of treating the cotton with sulphuric acid (0·25 per cent.) was found to be negligible; thus, the viscosity of the same sample of cotton before treatment was 0·42 unit, and afterwards 0·45 unit.

Many samples of cotton boiled on the manufacturing scale under various conditions have now been examined with the falling sphere viscosimeter, and several interesting relationships have been indicated. The large-scale work has proved conclusively that the conditions of the boiling process determine the viscosity of the purified cellulose, and it has been found possible by standardising these conditions to keep the viscosity of cotton-waste used for nitration within much narrower limits than heretofore. The results of the determination of the viscosity of one blend of cotton-waste, using different treatments, are given in table III.

TABLE III.

Solution.	Pressure of steam. Kilos. per sq. cm.	Time. Hours.	Viscosity of 2 per cent. solution.
2 per cent. NaOH 2 per cent. Na_2CO_3	Atmospheric.	10	317
2 per cent. NaOH 2 per cent. Na_2CO_3	,,	20	256
4 per cent. NaOH	,,	10	332
4 per cent. NaOH	,,	20	193
2 per cent. NaOH	1·4	10	240
2 per cent. NaOH	,,	20	94
1 per cent. NaOH 3 per cent. Na_2CO_3	2·8	10	172
2 per cent. NaOH 2 per cent. Na_2CO_3	,,	10	129
2 per cent. NaOH 2 per cent. Na_2CO_3	,,	20	19
2 per cent. NaOH	,,	10	73
2 per cent. NaOH	,,	20	24
4 per cent. NaOH	,,	10	48
4 per cent. NaOH	,,	20	4

These results again indicate the importance of temperature in reducing viscosity, and the influence of strength of solution is shown. It is also evident that sodium carbonate is ineffective compared with sodium hydroxide.

The experiments on different classes of waste given in table IV are of considerable interest. In these experiments, the conditions were the same in all cases, but the Eastern cottons give products the viscosity of which is about half that of American cotton of similar grade.

There is also a marked difference in the viscosity obtained with long-fibred cop-waste and short-fibred fly. It is hoped that further work in this direction will enable more definite correlations to be

made between climatic conditions of growth of cotton and the viscosity of solutions, and also between maturity of fibre and viscosity.

TABLE IV.

Treatment.—Ten hours under a pressure of 2·8 kilos. per sq. cm. with 4 parts of 3 per cent. sodium hydroxide solution to 1 part of cotton.

Material.	Viscosity of 2 per cent. solution.
American Fly	128
Eastern Fly	53
American Cops	57
Eastern Cops	26

A further relationship has been shown to exist between the viscosity of cellulose solutions and the viscosity of nitrocellulose solutions. The property inherent in cellulose to which viscosity is due is transmitted to the nitrated derivative. Table V indicates that high viscosity in the cellulose is accompanied by high viscosity in its derivative.

TABLE V.

Viscosity of cotton: 2 per cent. cuprammonium solution.	Viscosity of nitro-cotton: 5 per cent. solution in a mixture of ether and alcohol.
317	67
172	43
48	29
4	10

At the instance of Mr. F. R. Jackson, Director of the Flax Experimental Station at Selby, five samples of flax supplied by him were examined for viscosity by the falling sphere method. The results obtained are given in table VI.

TABLE VI.

	Viscosity of 1 per cent. solution.
A. Pond retted, hand scutched flax	22·3
B. As *A*, but twice scutched by machine	19·7
C. Twice retted in tanks under controlled conditions	30·2
D. Russian dew-retted, low grade	11·3
E. Originally scutched without retting, fibre then retted and re-scutched	26·5

These preliminary results indicate that the viscosity bears a relationship to the character of the flax; thus, Russian dew-retted, low-grade flax differs widely in viscosity from sample *C*, Selby flax, retted in warm water, and of far superior quality.

The viscosity-concentration curve for cellulose in cuprammonium has been studied, but Arrhenius's simple formula appears only to apply over short ranges of concentration.

A relationship between viscosity and solubility of cellulose in cuprammonium solution is indicated by observations made with a variety of cellulose.

The work has scarcely progressed far enough for wide generalisations to be made, but it seems clear that certain treatments can be applied to cellulose which alter its physical properties profoundly, but produce no decided change in chemical properties. This lends support to the view that the production of cellulose in the plant is a process of polymerisation, the older layers, presumably, being more highly polymerised than new growth; the process of boiling with sodium hydroxide may effect the reverse change and depolymerise the cellulose.

PART II.

[With LEO SPENCER and ROBERT McCALL.]

The Hydrogen Capillary Viscosimeter.

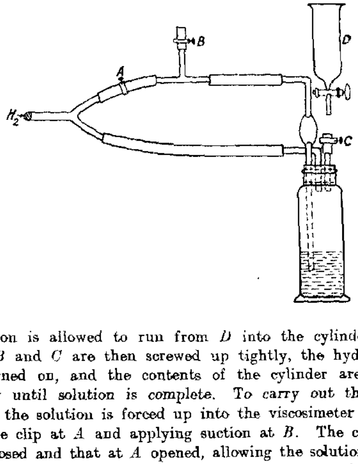
The chief difficulty with Ost's method of determination of viscosity is the progressive alteration which the solutions of cellulose undergo, changes in viscosity occurring all through the process of solution and up to the time of making the determination. Investigation showed that this change was caused by the presence of air and light, so a viscosimeter was devised in which solution of the cellulose was effected in an atmosphere of hydrogen and the influence of light was avoided. With this apparatus, concordant results were obtained, and it was possible to repeat determinations of viscosity of cellulose with satisfactory results. The apparatus consisted of: (1) a Kipp's hydrogen apparatus; (2) a washing bottle filled with sodium hydroxide solution to free the hydrogen from acid; (3) a glass cylinder of about 100 c.c. capacity to contain the cotton and cuprammonium solution, and a three-holed rubber stopper to fit; (4) a capillary viscosimeter, bulb 3—4 c.c., capillary of internal diameter 0·7 mm., length 12—15 cm.; (5) a tap funnel of 10 c.c. capacity to introduce the solution into the containing cylinders; (6) a supply of large glass beads.

The arrangement of the apparatus is shown in Fig. 2.

Procedure.—Half a gram of dry cotton is cut into small pieces to facilitate solution. The cotton, together with six or eight glass

beads, is introduced into the cylinder. The rubber cork containing the viscosimeter and inlet tubes is then inserted, and the air is displaced by a current of hydrogen whilst the cylinder is in an inverted position. A period of less than twenty minutes is necessary for complete displacement of air, and this is most essential, as even minute traces of air lower the viscosity of the cuprammonium solution of cotton. When the displacement of air is complete, 50 c.c. of cuprammonium solution are added in the following manner. The tap funnel, *D*, is attached to the capillary outlet tube at *C*, and the tap is opened for a few seconds to displace any air in the outlet tube and the connexion. The current of hydrogen is then stopped, the clip at *B* unscrewed, and

FIG. 2.



the solution is allowed to run from *D* into the cylinder. The clips at *B* and *C* are then screwed up tightly, the hydrogen is again turned on, and the contents of the cylinder are shaken vigorously until solution is complete. To carry out the determination, the solution is forced up into the viscosimeter bulb by closing the clip at *A* and applying suction at *B*. The clip at *B* is then closed and that at *A* opened, allowing the solution to fall in the capillary tube. The time of fall between two marks is then measured by a stop-watch. The measurement is repeated, with intervening shaking, until the results are seen to be constant, as it is sometimes difficult to tell by inspection whether solution has been complete. Brown paper covers for the cylinder and viscosimeter serve to protect the solution from the action of light. The

viscosimeter is standardised by means of a mixture of glycerol and water; the viscosity of this mixture is then compared with that of water in a viscosimeter of the Ostwald type of smaller bore.

Effect of Air on the Viscosity of Cellulose Solutions.

The following experiment indicates the effect of air on the viscosity of cuprammonium solutions of cellulose. A solution of cotton in cuprammonium was made in the presence of hydrogen, and the hydrogen was then displaced by air.

In one case the solution was allowed to remain without shaking, and in the second the solution was shaken continuously.

Time of contact with air in hours.	Viscosity: Water = 1	
	Standing only.	With shaking.
0	73	60
½	73	8
1	72	4
2	63	3
4	48	2·5
10	31	—
30	16	—
40	12	—

Effect of Light on Viscosity.

In this experiment, a solution of cotton in cuprammonium was made in the presence of hydrogen, and the viscosity was measured. The solution was then exposed to light. The following determinations were made at intervals:

Initial viscosity.	1376.	Water = 1.
After exposure to bright sunlight for 10 minutes	191	
After a further 4½ hours protected from light	186	
After further exposure for 10 minutes	84	
,, ,, ,, 15 ,,	56	
,, ,, ,, 30 ,,	38	
,, ,, ,, 75 ,,	27	

Use of the Falling Sphere Viscosimeter for Cuprammonium Solutions.

It appeared from the work with the hydrogen capillary viscosimeter that the falling sphere viscosimeter (see preceding paper) could be adapted for use with cuprammonium solutions of cellulose. It was necessary to use a narrower tube, 1 cm. in diameter, owing to the deep blue colour of the solution, otherwise the standard apparatus previously described was used.

As more viscous solutions could be dealt with advantageously, 2 per cent. solutions of cellulose in cuprammonium were used.

It was necessary to avoid contact with air during the solution of the cellulose. This is effected by placing 100 c.c. of cuprammonium solution with eight or nine glass beads in a stout, brown glass bottle of 150 c.c. capacity, and adding the weighed quantity of cotton. The bottle is then closed at once with an indiarubber stopper, through which a short capillary tube passes, one end being flush with the bottom of the stopper, the other end being connected by a short length of indiarubber tubing provided with a screw clip, to a second and similar bottle. The latter is closed with a rubber stopper through which pass two short glass tubes, one provided with a glass tap connecting it to the first bottle, the other connecting it by means of a short piece of pressure-tubing provided with a screw clip to the water-pump.

The connexion between the first and second bottle is closed by means of the tap, and the second bottle is exhausted by the pump; the screw clip between the second bottle and the pump is then closed and the glass tap is suddenly opened, when the rapid suction of air from the first bottle into the second causes bubbles to rise from the cuprammonium solution and to displace the air. This operation is repeated three times. The use of the second bottle ensures efficient and standard exhaustion of air without undue loss of ammonia. The screw clip attached to the first bottle, hitherto open, is now closed as tightly as possible, the bottle is detached, and immediately shaken vigorously for five minutes. The bottle is then immersed in a covered bath of water at 20° for eighteen to twenty-four hours with occasional shaking. The viscosimeter tube is filled from the bottle without access of air in the following manner. When solution is complete, the stopper is removed from the bottle without disturbing the liquid, and is replaced by a rubber stopper carrying a short inlet tube reaching to 1 cm. from the bottom of the bottle, and an outlet tube, diameter 5 mm., flush with the bottom of the stopper and about 50 cm. long, the inner end of which is capped by a cover of fine-meshed copper gauze. The viscosimeter tube, exactly 1 cm. diameter, is slipped over the long outlet tube, and the bottle is then inverted without shaking the liquid. The solution flows down into the viscosimeter tube, and, as the latter fills, the outlet tube is raised, but not above the surface of the liquid, care being taken to avoid air bubbles. With highly viscous solutions the flow is accelerated by the application of compressed air to the inlet tube of the bottle. When the tube is filled to within 3 cm. of the top the bottle is removed. The filled viscosimeter tube is then fitted

with a rubber stopper carrying a releasing tube for the steel balls, which should be exactly central. The viscosimeter tube is then placed in a vertical position in the water-bath at 20°, and the determination made by measuring the time of fall of a 0·15 cm. steel ball through 15 cm. With this method of filling, the measurement is made through solution which has not been exposed to air.

Calculation of Absolute Viscosity.

If the mean time of fall of the ball through 15 cm. is t, the absolute viscosity, η, is given by

$$\eta = 0{\cdot}42t,$$

the constant 0·42 including the correction factors. These are determined by calibration with castor oil of known viscosity, thus: Density of cellulose solution, 0·95; viscosity of standard sample of castor oil, 9·888, D 0·96; time of fall of ball through 15 cm. in 1-cm. tube, 23·4 sec.

$$\text{Constant} = \frac{\eta}{t} = \frac{\eta_1(s-\sigma)}{t_1(s-\sigma_1)} = \frac{9{\cdot}888 \times 6{\cdot}7}{23{\cdot}4 \times 6{\cdot}69} = 0{\cdot}423.$$

Study of the Cuprammonium Solution for Cellulose.

Although the main difficulties in the way of trustworthy determinations of the viscosity of solutions of cellulose in cuprammonium disappeared when the precautions used to avoid the action of light and air had been adopted, minor irregularities were still sometimes obtained, and as Ost's method for the preparation of the cuprammonium solution was being followed, this was eventually suspected as the cause of trouble. It was noticed that whilst duplicate experiments carried out on the same day gave results which were quite concordant, irregular results were obtained when an interval of some weeks was allowed to elapse before the duplicate experiment was carried out. A few extreme results may be given to indicate the nature of the discrepancies.

Cotton *A*.	Viscosity in Ost's solution	2·22
	Viscosity 3 weeks later..............	1·50
	Viscosity 6 weeks later..............	1·72
Cotton *B*.	Viscosity in Ost's solution	1·23
	Viscosity 6 weeks later..............	1·50

The analysis of various solutions showed that the variations in copper content were somewhat larger than would be expected from the examples given by Ost.

The extreme figures were:

Copper, grams per litre.	Ammonia, grams per litre.
15·1	196·4
11·6	225·2

When the copper and ammonia contents were intentionally varied widely, it was found that the viscosity of a sample of cotton was affected as follows:

Composition of solution, grams per litre.		Viscosity of cotton.
Cu.	NH_3.	
8·47	266·9	1·64
15·33	202·9	2·52
22·84	175·1	3·54
28·40	129·7	5·44

In the preparation of Ost's solution, besides the apple-green basic copper sulphate, two distinct precipitates are obtained, one pale blue and the other dark blue. Addition of water to the solutions containing these precipitates caused the dark blue needles gradually to dissolve, but left the pale blue precipitate undissolved.

The solutions were found to contain sulphate in quantities which increased as the concentration of the ammonia decreased. The dark blue needles, described by Ost as cuprammonium hydroxide, had the same crystalline form as tetrammine copper sulphate (Found: Cu = 25·84; SO_4 = 37·7. Calc.: Cu = 25·86; SO_4 = 39·1 per cent.). The pale blue precipitate was free from sulphate and was apparently copper hydroxide.

The precipitate of basic copper sulphate used by Ost to prepare his solution therefore appears to dissolve in ammonia as cuprammonium hydroxide and as tetrammine copper sulphate, any excess being left as tetrammine copper sulphate crystals and copper hydroxide.

To obtain further information, the solubilities of tetrammine copper snlphate in ammonia and copper hydroxide in ammonia were determined, with the following results.

Solubility of Tetrammine Copper Sulphate at 15° in Ammonia.

Cu, grams per litre.	NH_3, grams per litre.
0·43	234·1
1·13	222·1
2·37	192·9
3·46	175·8
5·16	153·7
7·66	145·3
11·11	134·0

The solubility of copper hydroxide in ammonia has been previously determined by Bonsdorff (*Zeitsch. anorg. Chem.*, 1904, **41**, 132) and Dawson (T., 1909, **95**, 370). In our work, the copper hydroxide was prepared by triturating basic copper sulphate with sodium hydroxide, as described by Dawson.

Solubility of Copper Hydroxide in Ammonia.

Solution	Cu, grams per litre.	NH_3, grams per litre.
A.	11·8	195·3
1st dilution	11·6	150·5
2nd ,,	11·0	132·5
3rd ,,	10·4	119·9
4th ,,	8·9	99·1
5th ,,	7·4	85·1
6th ,,	6·4	72·8
7th ,,	5·2	63·7
8th ,,	4·6	56·4
9th ,,	2·9	38·0
10th ,,	1·3	22·5
B.	12·2	205·2
1st dilution	12·1	176·4
2nd ,,	11·6	147·2
3rd ,,	9·6	112·8
4th ,,	7·8	95·9
5th ,,	6·4	77·7
6th ,,	5·2	60·8
7th ,,	4·0	46·2

The solubility of tetrammine copper sulphate in ammonia is a definite figure, since this substance is a definite crystalline compound, but the solubility of copper hydroxide seems to depend on the method of preparation adopted, and unless great precautions are taken, slight variations may be obtained even when one method of preparation is used, giving slightly variable solubility figures.

If the basic copper sulphate obtained by Ost's method behaves, on treatment with ammonia, as tetrammine copper sulphate and copper hydroxide, there will be a definite solubility of the tetrammine copper sulphate in ammonia of any particular strength and a solubility of copper hydroxide, which may vary owing to variations in the conditions of preparation of the basic copper sulphate. The use of an excess of basic copper sulphate should, therefore, give a solution in ammonia saturated with respect to tetrammine copper sulphate and with respect to copper hydroxide.

This was tested quantitatively in the following manner. A large excess of basic copper sulphate obtained by Ost's method was added to ammonia (D 0·880), and the whole kept in a thermostat at 15° in a tightly stoppered bottle for twenty-four hours and well shaken at intervals. The content of copper and ammonia in solution was then estimated. Additions of distilled water were then

ade, and after each addition the solution was shaken at 15° for venty-four hours before estimating the copper and ammonia gain. Two sets of experiments were carried out, and the results ere as follows:

Solution.	Cu, grams per litre.	NH_3, grams per litre.
riginal No. 1	11·0	267·1
fter 1st dilution..........	11·8	247·5
,, 2nd ,, ...	12·6	237·2
,, 3rd ,, ...	13·3	228·4
,, 4th ,, ...	15·7	207·0
,, 5th ,, ...	17·8	192·2
,, 6th ,, ...	19·4	182·0
,, 7th ,, ...	23·3	145·6
,, 8th ,, ...	26·4	129·7
riginal No. 2.	11·3	237·8
fter 1st dilution..........	13·5	218·0
,, 2nd ,, ...	14·6	206·7
,, 3rd ,, ...	16·7	194·4
,, 4th ,, ...	17·4	181·5
,, 5th ,, ...	17·6	171·7

The results obtained are not quite coincident, indicating the existence of different modifications of the basic copper salt, but the differences are scarcely larger than those obtained in the determination of the solubility of copper hydroxide in ammonia. This experiment confirms the impossibility of obtaining constant solutions by Ost's method, owing to the variation in solubility of copper hydroxide in ammonia.

If the solubility curves of basic sulphate, tetrammine copper sulphate, and cupric hydroxide are considered together, it will be seen (Fig. 3) that the solubility curve for basic copper sulphate represents a solution saturated with both tetrammine copper sulphate and copper hydroxide, the solubility being the sum of the solubility of tetrammine copper sulphate and of the solubility of some modification of copper hydroxide, as the general form of the curve and the value of the solubility found is consistent with this view.

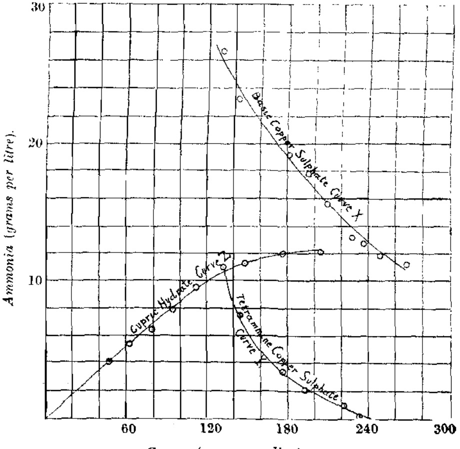
The study of Ost's cuprammonium solution described above rendered it evident that the precise adjustment of this solution to definite concentration of copper and ammonia would be difficult, and as it was apparent that the value of the viscosity obtained for a sample of cotton depended to an appreciable extent on the concentration of ammonia and copper in the solution, Ost's method of preparation of the solution was abandoned.

Since copper hydroxide prepared by Dawson's method showed a fairly definite solubility in ammonia, an unsaturated solution of this form of copper hydroxide was chosen as the standard cuprammonium solution.

The method adopted was the following. Sixty grams of copper sulphate are dissolved in 1 litre of hot water, a few drops of sulphuric acid added, the solution is allowed to cool to 50°, and ammonia (D 0·880) added until the precipitation of basic copper sulphate is complete, any excess of ammonia being neutralised with a few drops of sulphuric acid. The precipitated basic sulphate is allowed to settle, and the supernatant liquid decanted.

FIG. 3.

Solubilities in ammonia at 15°.



The precipitate is washed by decantation with hot water, 200 c.c. of 20 per cent. sodium hydroxide solution are added, and the whole is well shaken at the ordinary temperature. The precipitate is converted into blue cupric hydroxide, which is then allowed to settle, the supernatant liquid decanted, and the precipitate washed by decantation with cold water until the filtrate is free from alkali and sulphate. The precipitate is then collected, washed with distilled water, and dried on a porous plate at 40°,

The dried cupric hydroxide is transferred to an aspirator bottle and 800 c.c. of ammonia, containing 200—210 grams of ammonia per litre, are added. The whole is well shaken and the excess of cupric hydroxide allowed to settle. The supernatant liquid is run off through a glass wool filter and the volume measured. The copper in the solution is determined, and the theoretical quantity of ammonia is added to give a solution containing 11 grams of copper and 200—210 grams of ammonia per litre.

The composition of the finished solution is finally checked by analysis.

Trouble may be experienced in preparing this solution unless the conditions laid down are strictly maintained.

This work was carried out at the Research Department, Royal Arsenal, Woolwich, and is published by permission of the Director of Artillery, War Office, to whom our thanks are due. We also desire to express our thanks to Lieut.-Colonel R. A. Craig, C.M.G., and to Sir Robert Robertson, K.B.E., F.R.S., for the interest they have shown in this work.

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LIII.—*The Influence of the Solvent on the Velocity of Reaction between certain Alkyl Iodides and Sodium β-Naphthoxide.*

By Henry Edward Cox.

From the literature relating to the influence of the solvent on velocity of reaction, it is apparent that no satisfactory connexion between the physical or chemical properties of the solvent and its effect on velocity-constants has yet been deduced. Theories which are in agreement with the observations in one reaction are found to be quite at variance with facts when the same solvents are examined in relation to another reaction.

The most obvious supposition, based on the Nernst-Thomson rule, that the velocity would be greatest in solvents of highest dielectric constant, is satisfactory in the case of certain reactions investigated by Menschutkin (*Zeitsch. physikal. Chem.*, 1887, **1**, 611; 1890, **6**, 41), but it is quite useless in the case of a large

number of other reactions, even those in which the reaction is probably between ions.

A comprehensive theory by van't Hoff ("Vorlesungen," 1901, 1. 214), in which the action of the solvent is attributed to displacement of the equilibrium of the reacting system—depending on solubility relations—and a possible specific effect, has been found to be in accord with the facts in certain isomeric changes investigated by Dimroth (*Annalen*, 1910, **377**, 127), but attempts to apply it to other reactions fail. It is therefore evident that specific catalytic effects quite outweigh the effects of displacement of equilibrium.

There is also no evidence that viscosity of the solvent has any great influence on the velocity-constants; experiments by Reformatsky (*Zeitsch. physikal. Chem.*, 1891, **7**, 34) and others show that velocity is not decreased by increasing viscosity.

The only generalisation that appears to be supported by most of the available data is that of Patterson and Montgomerie (T., 1912, **101**, 26, 2100), who state that "it appears that solvents influence quite different reactions in a uniform manner; although the manifestation of this effect may be of an opposite character, a given set of solvents may hasten a particular reaction in a certain sequence, whilst in the same, or nearly the same, sequence they retard another reaction. The property or properties which bring this about are probably the same throughout."

Several examples of this are to be found in the literature, and some are quoted by Patterson and Montgomerie. It is considered by several authorities that in many or all cases some combination occurs between solvent and solute, with the formation of additive compounds of an unstable kind. On the radiation theory (compare Baly, "Spectroscopy," 1918, 491), this gives rise to a field of force in the surrounding ether, which is opened by the absorbable radiation, with consequent increase in chemical activity.

On these views, it is not unreasonable to expect that there might be some connexion between the chemical constitution of a solvent and its effect on the velocity of any particular reaction. It is therefore of interest to examine the influence of a series of related solvents in the hope of tracing some connexion between the constitution and the effect on the velocity. For the particular reactions here discussed, the alcohols form a convenient series from considerations of solubility.

The velocity-constants of the reactions between methyl, ethyl, and *n*-propyl iodides and sodium β-naphthoxide have therefore been measured in the following fifteen alcohols: methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec.*-, and *tert.*-butyl, *n*-, *iso*-, *sec.*-, and *tert.*-

myl, allyl and benzyl alcohols, and ethylene glycol (as an example f a dihydric alcohol). The influence of concentration has been ueasured in four of them, and the effect of water has been studied. 'he alcohols afforded opportunity of observing the effect of structure in the different isomerides as well as the regular effect of ncreasing molecular weight in a homologous series. No complication arises except the possible alcoholysis discussed below and he increasing constant in the case of *tert*.-amyl alcohol. Sodium β-naphthoxide is readily soluble in the alcohols, but it is only very sparingly so in neutral or acidic solvents of the associating type. No results appear on record for a series of alcohols or other homologous series, although a number of observations are recorded on ethyl, methyl, *iso*butyl, and benzyl alcohols; these are often in the same increasing or decreasing order as stated by Patterson and Montgomerie.

Some account of the reaction between the alkyl iodides and sodium naphthoxides has been given in previous papers (T., 1918, **113**, 666, 821), and it has been shown that the reactions are bimolecular, but that the constant is dependent on the initial concentration. In a series of solvents here described, the reaction has been fouud to be regular in all cases, and satisfactory values of the velocity-constant are obtained.

In *tert*.-butyl and *tert*.-amyl alcohols, however, there is a gradual increase in the value of k for methyl iodide as the reaction proceeds, so that it is necessary to measure only a small part of the reaction to obtain a satisfactory constant. This is apparently due to the low solubility of the products of the reaction, which are precipitated after a short time, the velocity of reaction then increasing.

EXPERIMENTAL.

The Influence of the Solvent on the Velocity of Reaction at 50·5°.

The method of preparation of sodium β-naphthoxide given in the previous paper has been improved. Sodium is dissolved in recently boiled absolute alcohol, the calculated quantity of dry β-naphthol added, and the solution evaporated to dryness in a vacuum. The product is dissolved in the smallest possible quautity of boiling acetone; the flask is corked while the solution is still, boiling, and immediately cooled; the salt then crystallises in minute lamellæ ($C_{10}H_7ONa,C_3H_6O$), and is filtered rapidly, washed with cold acetone, then dried at 150° in a current of hydrogen. Sodium β-naphthoxide obtained in this way is quite white.

The method of measuring the velocity was the same as before. special pipettes being made to work with very small quantities of

the more expensive solvents. In each experiment the initial concentration is N with respect to naphthoxide and iodide, and the temperature is 50·5°.

The values of k are in good agreement in each experiment, and in many cases duplicate determinations have been made. For economy of space, only a few typical experiments will be given in full, and the other results summarised. The unit of time is one minute and of concentration one gram-molecule per litre.

Normal Primary Alcohols.

Methyl, ethyl, and *n*-propyl alcohols were in each case dehydrated over calcium oxide and calcium, and finally distilled from fresh calcium turnings. *n*-Butyl alcohol was fractionated several times from "fermentation" butyl alcohol, then dehydrated with potassium carbonate and, finally, quicklime, and again fractionated. It boiled at 116—116·5°/756 mm. *n*-Amyl alcohol was from Kahlbaum.

n-*Propyl Alcohol.*

N-Ethyl iodide; N-Naphthoxide. 0·500 C.c. titrations, N/25-HCl.

t.	$a-x$.	k.
0	11·70	—
9	10·55	0·0129
16	9·80	0·0127
24	9·10	0·0127
32	8·40	0·0131
41	7·95	0·0123
	Mean	0·0127
	(Duplicate	0·0129).

n-*Butyl Alcohol.*

N-Methyl iodide; N-Naphthoxide; 0·500 C.c. titrations, N/25-HCl.

t.	$a-x$.	k.
0	10·65	—
3	9·40	0·0520
6	8·40	0·0524
9	7·60	0·0523
12	6·85	0·0542
15	6·35	0·0530
	Mean	0·0528.

TABLE I.

Summary of Results.

Solvent.	Methyl iodide.	Ethyl iodide.	*n*-Propyl iodide.
Methyl alcohol	0·0459	0·0130	0·00567
Ethyl alcohol	0·0941	0·0212	0·00859
n-Propyl alcohol	0·0643	0·0127	0·00507
n-Butyl alcohol	0·0528	0·0107	0·00379
n-Amyl alcohol	0·0298	0·00518	0·00194

On consideration of the above results for normal alcohols, it is apparent that, with the exception of methyl alcohol, which is subnormal, there is a gradual and fairly regular decrease in the value of k with increasing molecular weight; this is well shown on plotting a curve, velocity-constant–molecular weight (see Fig. 1). This suggests that the influence is partly additive as well as a

constitutive property, as the addition of a CH_2-group has a regular retarding action, which somewhat diminishes as the series is ascended.

There is a striking similarity in this curve to that of Burke and Donnan (T., 1904, **85**, 555), who, in their investigation of the reaction between silver nitrate and alkyl iodides, found a similar effect of the methyl group in the activity of the iodides, and this goes to show that methyl alcohol is subnormal in its action as solvent; its normal position should be far above ethyl alcohol (compare the curves given for Menschutkin's and Hecht and Conrad's data by Segaller, T., 1913, **103**, 1154).

It may be remarked that in a large number of reactions recorded the velocity in ethyl is greater than in methyl alcohol, and the opinion is expressed by Senter (T., 1916, **109**, 686) that, in general, reactions should be faster in methyl alcohol, which he attributes to the higher viscosity of ethyl alcohol.

In a number of other reactions, however, methyl alcohol is the more favourable medium, and the above results suggest that this subnormal activity in certain reactions may be one of the frequently observed irregularities of the first member of a homologous series. Sodium ethoxide, phenoxide, and α- and β-naphthoxides all react more rapidly in ethyl alcohol.

Although the influence of these solvents is similar in each case, there are minor differences; thus, it appears from the following tables of the relative values in the solvents that the three iodides are not affected equally; ethyl and *n*-propyl iodides are more affected than is methyl iodide.

This is shown in table II by expressing the velocities in terms of the velocity in *n*-amyl alcohol.

TABLE II.

Solvent.	Methyl iodide.	Ethyl iodide.	*n*-Propyl iodide.
Methyl alcohol	1·54	2·51	2·92
Ethyl alcohol	3·16	4·09	4·43
n-Propyl alcohol	2·16	2·45	2·61
n-Butyl alcohol	1·77	2·06	1·95
n-Amyl alcohol	1·00	1·00	1·00

The differences become more marked in some of the other solvents dealt with in this paper.

iso-, sec.-, *and* tert.-*Alcohols.*

*iso*Propyl, *sec.*-amyl (methylpropylcarbinol), and *tert.*-butyl alcohols were Kahlbaum's preparations dehydrated over quicklime.

*iso*Butyl alcohol was fractionated from the commercial product and boiled at 107·5—109°; *sec.*-butyl alcohol was prepared by a Grignard reagent and boiled at 99·5—100·5°. *iso*Amyl alcohol was purified from *sec.*-butylcarbinol by preparing potassium amyl sulphate and crystallising; after dehydrating, it distilled at 131—132°, and had $[\alpha]_D^{15}$ less than 0·5°. *tert.*-Amyl alcohol was prepared by Adams, Kamm, and Marvel's method (*J. Amer. Chem. Soc.*, 1918, **40**, 1950), and boiled at 102—103°.

The results of the velocity experiments are all in satisfactory agreement, as illustrated below, with the exception that, in *tert.*-butyl and *tert.*-amyl alcohols, methyl iodide shows a gradual increase, due, apparently, to insolubility of the naphthyl methyl ether; these figures are given in the examples below:

sec.-*Propyl Alcohol.*

N-Propyl iodide; *N*-Naphthoxide. 0·500 C.c. titrations, *N*/25-HCl.

t.	*a*−*x*.	*k*.
0	12·00	—
21	10·65	0·00629
34	9·95	0·00631
51	9·25	0·00607
64	8·70	0·00617
75	8·30	0·00619
	Mean *k*........	0·00621

Methylpropylcarbinol.

N-Methyl iodide; *N*-Naphthoxide. 0·112 C.c. titrations, *N*/100-HCl.

t.	*a*−*x*.	*k*.
0	10·50	—
2	9·90	0·0323
5	9·15	0·0315
8	8·50	0·0314
11	7·65	0·0361
14	7·20	0·0349
	Mean *k*........	0·0332

tert.-*Butyl Alcohol.*

N-Methyl iodide; *N*-Naphthoxide. 0·112 C.c. titrations, *N*/100-HCl.

t	*a*−*x*.	*k*.
0	10·40	—
3	9·50	0·0341
7	8·65	0·0311
9	7·85	0·0389
12	6·85	[0·0465] omitted.
0	10·45	—
5	9·20	0·0325
8	8·40	0·0365
10	8·00	0·0366
	Mean *k*........	0·0352

tert.-*Amyl Alcohol.*

N-Methyl iodide; *N*-Naphthoxide. 1·00 C.c. titrations, *N*/25-HCl.

t.	*a*−*x*.	*k*.
0	24·50	—
20	20·20	0·0109
27	19·05	0·0108
34	17·50	0·0120
40	16·70	0·0119
	Mean *k*........	0·0114.

The results obtained in these alcohols are summarised below.

TABLE III.

Solvent.	Methyl iodide.	Ethyl iodide.	Propyl iodide.
*iso*Propyl Alcohol	0·0975	0·0177	0·00621
*iso*Butyl ,, ...	0·0635	0·0113	0·00374
sec.-Butyl ,, ...	0·0571	0·0107	0·00370
tert.-Butyl ,, ...	0·0350	0·00501	0·00149
*iso*Amyl ,, ...	0·0392	0·00649	0·00199
sec.-Amyl ,, ...	0·0332	0·00461	0·00167
tert.-Amyl ,, ...	0·0114	0·00155	0·000525

These results show the same diminution of the velocity-constant as the series is ascended in the same class of alcohol; thus, the velocity decreases regularly in the series *iso*propyl, *iso*butyl, *iso*amyl, similarly with the series of secondary and tertiary alcohols.

This is clearly seen in Fig. 1, which shows the *iso*-alcohols; the effect of increasing molecular weight is very similar in the four classes of alcohols. It is also apparent from the table of results or the figures that the *iso*-alcohols are in each case more favourable media than their normal isomerides; similarly, the secondary alcohols are more favourable solvents than the tertiary alcohol of the same molecular weight, but are slightly less active than the corresponding *iso*-alcohol. For a given molecular weight, therefore, the order of decreasing activity is: *iso*, secondary, normal, tertiary. Thus, with methyl iodide the figures are:

*iso*Butyl alcohol	0·0635	*iso*Amyl alcohol	0·0392
sec.-Butyl alcohol	0·0571	*sec.*-Amyl alcohol......	0·0332
n-Butyl alcohol	0·0526	*n*-Amyl alcohol	0·0298
tert.-Butyl alcohol......	0·0350	*tert.*-Amyl alcohol......	0·0114

(In the reaction with ethyl and *n*-propyl iodides the figures are very near together in the amyl alcohols, and there appears to be a small divergence from this order.)

In connexion with these results, the following points may be noted. In all three classes of alcohols, the increasing number of carbon atoms in a straight chain decreases the activity as solvent; a branching chain in the primary alcohols produces a distinct rise in activity, so much so that the constant approximates to that of the next higher normal primary alcohol. The introduction of a methyl group into the carbinol group produces, first, a rise (secondary alcohols) and then a larger fall (tertiary alcohols).

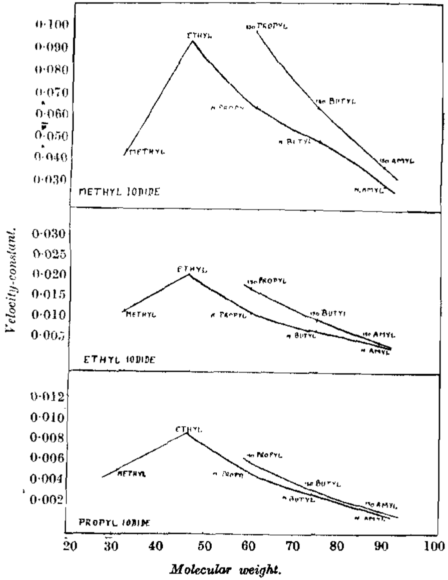
It may be remarked that these observations are in the opposite order to the activity of the corresponding alkyl iodides as measured by velocity of etherification with sodium phenoxide (Segaller, *loc. cit.*), it having been found that *iso*- and *sec.*-alkyl iodides are less

reactive than the normal isomerides, and tertiary iodides much more reactive.

Allyl and Benzyl Alcohols and Ethylene Glycol.

These alcohols have been included specially to observe the effect of unsaturation, a benzene ring, and a second hydroxyl group respectively. The reaction in these solvents is quite normal.

FIG. 1.



Normal and iso-alcohols.

On account of the high viscosity of glycol, a special pipette was calibrated with no constriction at the outlet; it was rinsed out

each time with water; in this way, the quantity delivered is satisfactorily constant.

Allyl alcohol was distilled from calcium oxide immediately before use (b. p. 94—95°). Benzyl alcohol was the commercial product redistilled three times (b. p. 205·5°), and ethylene glycol was prepared in the usual way from ethylene dibromide; it boiled at 197°. The experimental data are exemplified by the reaction with ethyl iodide in glycol:

N-Ethyl iodide. 0·129 C.c. titrations.		*N*-Naphthoxide. *N*/100-HCl.
t.	*a*−*x*.	*k*.
0	12·40	—
15	10·25	0·0145
23	9·45	0·0141
30	8·90	0·0136
40	8·00	0·0143
	Mean k	0·0141

*In the case of methyl and ethyl iodides, the mixture is homo*geneous up to about one-half the reaction, after which time the ether begins to separate out. With propyl iodide, the reaction proceeds to about two-thirds before separation of the products.

TABLE IV.

Summary of Results in these Solvents.

Solvent.	Methyl iodide.	Ethyl iodide.	Propyl iodide.
Allyl alcohol	0·0381	0·00562	0·00195
Benzyl alcohol	0·0357	0·00781	0·00242
Ethylene glycol..........	0·0578	0·0141	0·00431

It is remarkable that the velocity-constants are of similar magnitude in three such different solvents; the figures are quite comparable with propyl and amyl alcohols, already discussed.

Allyl alcohol was specially selected because of its well-known similarity in physical properties to *n*-propyl alcohol, and the fact that the constants are distinctly different (about one-half) from those in the latter solvent is very suggestive that the solvent influence is largely chemical rather than physical; the boiling point, dielectric constant, and refractive index (which is important from the point of view of the radiation hypothesis) are almost identical, yet the introduction of a double bond makes more difference in the velocity than there is between *n*- and *iso*-propyl alcohols. This supports the idea that the solvent participates in a *chemical reaction.*

A comparison of the figures for benzyl alcohol brings out the

fact that the velocity-reducing effect of a number of carbon atoms when in the form of the benzene ring is less than that of a similar number in a straight chain, for the value of k is somewhat higher than that of *n*-amyl alcohol with four carbon atoms attached in a chain to the carbinol group. It may be remarked, too, that in much work in which benzyl alcohol has figured it is a more favourable medium than some of the aliphatic alcohols, notably *iso*amyl alcohol.

Ethylene glycol illustrates the effect of a second hydroxyl group; on comparing it with ethyl alcohol, it is seen that the exchange of hydrogen for hydroxyl considerably reduces the activity of the solvent, and its effect is not much different from *n*-propyl alcohol, so that the introduction of a hydroxyl gronp is similar in result to the introduction of another CH_2-group.

There is, however, nothing to show the influence of solubility, which is so different in glycol and ethyl alcohol.

Influence of Water on the Velocity of Reaction.

Water should take the first place in a list of alcohols, but it is not possible to measure the velocity of these reactions in it, because the alkyl iodides are not sufficiently soluble, but the effect of water on the velocity has been found to be very considerable in many reactions. For this reason, the effect of water on the velocity of the reaction with ethyl iodide in ethyl alcohol has been investigated, with the following results:

TABLE V.

Ethyl Alcohol.

Percentage by weight.	k.
100	0·0212
90	0·0227
80	0·0255
70	0·0241
60	0·0206

In 50 per cent. alcohol, the naphthyl ethyl ether separates early in the reaction, and the velocity at once increases; below 50 per cent., the alkyl iodide is not soluble to N-concentration. It is seen from these results that the addition of water at first accelerates the reaction, a maximum being reached in the vicinity of 80 per cent. alcohol; thereupon the further addition of water retards the velocity.

It may be remarked that Miss Burke and Donnan made a similar observation with silver nitrate (*Zeitsch. physikal. Chem.*, 1909,

69, 163). No explanation has been suggested, but it is possible that side reactions take place in the case of aqueous-alcoholic sodium naphthoxide, as this substance undergoes hydrolysis in water and probably alcoholysis in ethyl alcohol.

The Influence of the Solvent on the Relative Activity of the Alkyl Iodides, and Comparison of Sodium Ethoxide, Phenoxide, and Naphthoxide.

The previous pages show that there is no inversion of the order of activity of the three alkyl iodides by influence of the solvent, but it is noticeable that the order of the activity of the solvents is not quite the same. Table VI shows the relative activity in the above solvents in terms of the slowest (namely, *tert.*-amyl alcohol), and columns 4, 5, and 6 show the relative activity of the three iodides in each solvent in terms of propyl iodide in that solvent. For example, it is seen that methyl iodide is from eight to twenty-four times as reactive as propyl iodide, according to the solvent, and the influence of the solvent is greater on propyl iodide than on methyl iodide.

TABLE VI.

Solvent.	Methyl iodide.	Ethyl iodide.	Propyl iodide.	Methyl iodide.	Ethyl iodide.	Propyl iodide.
*iso*Propyl alcohol	8·55	11·41	11·84	15·70	2·85	1·00
Ethyl ,, ...	8·25	13·69	16·38	10·95	2·47	1·00
n-Propyl ,, ...	5·64	8·20	9·65	12·68	2·50	1·00
*iso*Butyl ,, ...	5·57	7·30	7·13	16·96	3·02	1·00
Glycol	5·07	9·10	8·21	13·41	3·27	1·00
sec.-Butyl ,, ...	5·01	6·90	7·05	15·45	2·90	1·00
n-Butyl ,, ...	4·63	6·90	7·22	13·93	2·82	1·00
Methyl ,, ...	4·02	8·39	10·80	8·13	2·29	1·00
*iso*Amyl ,, ...	3·44	4·18	3·79	19·70	3·26	1·00
Allyl ,, ...	3·34	3·63	3·72	19·54	2·88	1·00
Benzyl ,, ...	3·13	5·04	4·61	14·75	3·23	1·00
tert.-Butyl ,, ...	3·07	3·23	2·84	23·49	3·36	1·00
sec.-Amyl ,, ...	2·91	2·98	3·18	19·88	2·70	1·00
n-Amyl ,, ...	2·62	3·34	3·70	15·37	2·67	1·00
tert.-Amyl ,, ...	1·00	1·00	1·00	21·71	2·95	1·00

In ethyl alcohol as solvent, it is possible to compare the activity of sodium ethoxide, phenoxide, and naphthoxide, as these have all been measured with the alkyl iodides (Hecht Conrad and Brückner, and Segaller); the figures for ethoxide and phenoxide are calculated from the data of these authors. At 42·5°, the relative activity of β-naphthoxide as compared with phenoxide is:

Methyl iodide	1·4
Ethyl ,, ...	1·4
Propyl ,, ...	1·5

which shows that the relative activity of these bases is constant and independent of the iodide with which it is measured. The following figures show that when ethoxide is compared with phenoxide and naphthoxide, the activity is not independent of the iodide.

$(t = 40 \cdot 0°)$.	$\frac{\text{Ethoxide}}{\beta\text{-Naphthoxide}}$.	$\frac{\text{Ethoxide}}{\text{Phenoxide}}$.
Methyl iodide	5·3	7·4
Ethyl ,, ...	1·9	2·7
Propyl ,, ...	1·5	2·2

The Effect of Initial Concentration in Various Solvents.

In the previous papers already referred to, it has been shown that the velocity of reaction of the alkyl iodides with sodium naphthoxide is dependent on the initial concentration of the base. In ethyl alcohol, the velocity has been shown to be decreased in accordance with Hecht and Conrad's equation, $k_v = k_1 + a \log v$.

The work of Acree and his co-workers (see Shroder and Acree, T., 1914, **105**, 2582) shows that sodium ethoxide and phenoxide are very much ionised in alcoholic solution, and that both the ions and the molecules take part in the reaction with alkyl iodides, and that with different velocities.

It is reasonable to suppose that a similar phenomenon takes place with naphthoxide (boiling-point determinations by the author show evidence of dissociation), which makes it probable that this increase is due to the increasing ionisation, and, consequently, increasing proportion of the reaction due to ions instead of molecules. It has also been shown that at higher dilutions the velocity-constant increases abnormally rapidly with methyl iodide in ethyl alcohol.

A similar increase—first regular, then abnormal—is now observed in methyl alcohol, and it is convenient to discuss these two solvents separately, because in them the question of alcoholysis arises, and

TABLE VII.

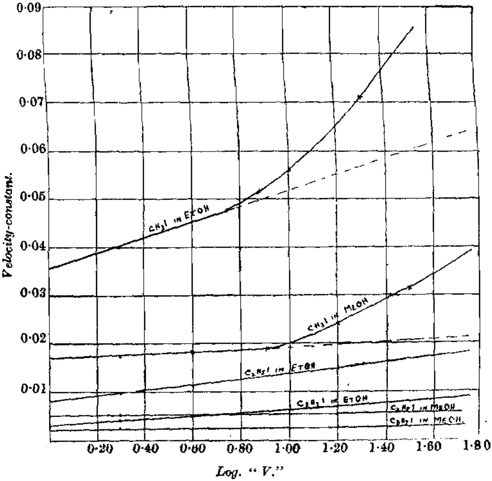
Methyl Iodide and Sodium β-Naphthoxide in Equivalent Concentration. $t = 40 \cdot 0°$.

v.	k_v (found).	k_v (calculated).
1	0·0164	0·0164
2	—	0·0171
4	0·0170	0·0179
8	0·0183	0·0186
16	0·0242	0·0194
32	0·0313	0·0201
64	0·0369	0·0209

" a " = 0·0025.

experiments have been made with a view to gain information on this point. The results obtained for the three iodides and sodium β-naphthoxide in methyl alcohol are shown in tables VII and VIII and illustrated in Fig. 2. It will be seen that the same phenomena appear in both these solvents; the figures in ethyl alcohol have already been given (T., 1918, **113**, 666).

Fig. 2.



Sodium β-naphthoxide and the alkyl iodides in methyl and ethyl alcohols.

TABLE VIII.

	Ethyl Iodide.		*Propyl Iodide.*	
v.	k_v (found).	k_v (calc.).	k_v (found).	k_v (calc.).
1	0·00460	0·00460	0·00202	0·00202
4	0·00293	0·00496	0·00233	0·00238
16	0·00539	0·00532	0·00277	0·00274
32	0·00551	0·00550	0·00299	0·00292
	"*a*" = 0·00060		"*a*" = 0·00060.	

The figures are very similar to those obtained for sodium α-naphthoxide; the latter, however, is slightly more reactive; thus, at N-concentration in methyl alcohol, k_α/k_β is:

Methyl iodide..................	1·00
Ethyl iodide	1·16
Propyl iodide..................	1·17

The work of Acree and others in connexion with sodium ethoxide and phenoxide shows that the velocity increases with decreasing concentration, because the reaction is between ions and molecules of the base and the non-ionised alkyl iodide; the velocity of the ionic reaction is greater than that of the molecular reaction, so that as the ionisation increases with dilution, so does the velocity increase. Shroder and Acree show, in the paper already quoted, that the increase of ionisation is according to the empirical equation of Hecht and Conrad.

In considering the cause of the abnormal increase in activity of methyl iodide at higher dilutions in both methyl and ethyl alcohols, it is to be expected that if it were due to a property of the naphthoxide, it would appear also with the other alkyl iodides. Some evidence has been obtained which suggests that sodium β-naphthoxide undergoes alcoholysis in dilute solution, and this hypothesis affords an explanation of the phenomena observed, but, owing to the experimental difficulty of detecting traces of ethyl ether in a complex alcoholic mixture, conclusive evidence has not been obtained.

The formation of ether is possible in two ways: (1) by alcoholysis, in which case the reactions are: (*a*) $C_{10}H_7{\cdot}ONa + EtOH \rightleftharpoons C_{10}H_7{\cdot}OH + EtONa$; (*b*) $EtONa + EtI \longrightarrow Et_2O + NaI$; (2) by alkylidene dissociation (alkylene dissociation is impossible with methyl iodide).

The latter possibility (Nef, *Annalen*, 1899, **309**, 126) has been critically examined by Miss Burke and Donnan (T., 1904, **85**, 555), and shown to be unsatisfactory; also, if it occurred with naphthoxide, it would be expected with phenoxide, ethoxide, and other bases.

The velocity of reaction between sodium ethoxide and the alkyl iodides is greater than that of sodium naphthoxide, so that if alcoholysis takes place, a higher value of k will be obtained at the commencement of a reaction than at the end, when the increasing concentration of free naphthol retards further alcoholysis. In this case, the effects would be expected in the case of each of the three alkyl iodides, but examination of the velocity-constants shows that a small amount of alcoholysis would not be detected in this way The following table shows the velocity-constants of methyl,

hyl, and propyl *iodides* with *sodium ethoxide at* 40·0° (solvent, thyl alcohol), calculated from the data of Hecht, Conrad, and rückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289).

TABLE IX.

	Methyl iodide.		Ethyl iodide.		Propyl iodide.	
	Ethoxide.	Naphth-oxide.	*Ethoxide.*	Naphth-oxide.	Ethoxide.	Naphth-oxide.
1	0·188	0·0356	0·0148	0·00790	0·00483	0·00316
2	0·214	0·0406	0·0175	0·00991	0·00597	—
5	0·248	0·0473	0·0211	0·0116	0·00747	0·00536
10	0·273	0·0559	0·0238	0·0140	0·00841	0·00653
20	0·299	0·0721	0·0265	0·0157	0·00971	0·00739
40	0·323	—	0·0292	0·0170	0·01089	0·00852

The constants for methyl iodide and ethoxide are five times greater than those of sodium β-naphthoxide and the same iodide, out those with ethyl and propyl iodides with ethoxide are only 1·7 and 1·5 times the corresponding figures with naphthoxide. As the values are so nearly the same with the latter iodides, it is clear that a very small amount of ethoxide produced by alcoholysis would produce so small a change in the value of k that its effect would not be observed.

The following experiments show the effect of sodium ethoxide on the reaction; the amount added is larger than that likely to be produced by alcoholysis.

Experiment 1.—Solvent, ethyl alcohol, $t = 40·0°$, $N/8$-methyl iodide, $N/10$-sodium naphthoxide, $N/40$-sodium ethoxide.

Experiment 2.—Solvent, ethyl alcohol, $t = 40·0°$, $N/8$-ethyl iodide, $N/10$-sodium naphthoxide, $N/40$-sodium ethoxide (these are equivalent to $N/8$-ethoxide and $N/10$-β-naphthol). Acid = $N/25$-HCl, 5·0 c.c. titrations.

1.

t.	$a-x$.	k.	k'.
0	15·25	—	—
10	13·75	0·0894	0·0894
25	12·10	0·0854	0·0826
42	11·00	0·0792	0·0689
62	9·85	0·0725	0·0604
102	8·50	0·0638	0·0503
150	7·30	0·0595	0·0503

2.

t.	$a-x$.	k.	k'.
0	15·55	—	—
62	13·75	0·0170	0·0170
120	12·60	0·0164	0·0157
180	11·40	0·0163	0·0161
284	9·95	0·0159	0·0154
363	9·05	0·0159	0·0158
440	8·35	0·0158	0·0151
Mean		0·0162	

Experiment 3.—Solvent, methyl alcohol, $t = 40·0°$, $N/8$-methyl iodide, $N/10$-sodium naphthoxide, $N/40$-sodium methoxide. Acid = $N/30$-HCl, 5·0 c.c. titrations.

t.	$a-x$.	k.	k'.
0	18·55	—	—
17	17·40	0·0286	0·0286
33	16·60	0·0288	0·0288
54	15·65	0·0276	0·0261
85	14·50	0·0266	0·0246
115	13·65	0·0262	0·0214
145	12·90	0·0245	0·0212

In these experiments, the figures in the fourth column (k') are obtained by calculation from each pair of titrations; this shows the course of the reaction and the decrease in k more clearly than the figures in the third column, which are referred to t_0 in the usual way. Experiments 1 and 3 show a similar course in both methyl and ethyl alcohols. At the commencement of the reaction, k is much increased (nearly doubled in ethyl alcohol), and rapidly diminishes as the free ethoxide is used up; then it falls to a value approximating that of $N/10$-naphthoxide. In Experiment 2, the course of the reaction with ethyl iodide is seen; here the presence of ethoxide has no apprecable effect on the velocity-constant after the first titration, and even in that the effect is not large. These experiments show that alcoholysis increases the mean velocity-constant with all the iodides, but that a small amount of alcoholysis does not show a marked diminution in k as a reaction proceeds, and is so small that with the higher alkyl iodide its effect would be unnoticeable. It is therefore suggested that in dilute alcoholic solution, sodium naphthoxide undergoes alcoholysis to a small extent, and this occasions the observed increase with methyl iodide at high dilutions.

Further experiments were made with the object of detecting ethyl ether in the products of the reaction; in the author's opinion ether was present, but owing to the experimental difficulty it has not been definitely proved.

The influence of initial concentration has also been measured in *iso*butyl and benzyl alcohols. In these solvents, the effect is very large; in the case of ethyl and propyl iodides, the velocity is nearly doubled by changing the initial concentration from N to $N/8$, yet, as will be seen from the examples already given, there is no important rise in the velocity-constant during any one experiment, although in many cases more than half the reaction was measured. It may be suggested that the negative catalytic effect of the product of the reaction may just balance the increasing velocity due to the decreasing concentration of the reacting substances.

*iso*Butyl and benzyl alcohols are much more associated substances than methyl and ethyl alcohols, and it may be that the

reacting ions or molecules are associated with the solvent molecules.

The experimental results are as follows.

TABLE X.

	Methyl iodide.		Ethyl iodide.		Propyl iodide.	
v.	*iso*Butyl.	Benzyl.	*iso*Butyl.	Benzyl.	*iso*Butyl.	Benzyl.
1	0·0232	0·0125	0·00399	0·00273	0·00135	0·000884
4	0·0263	0·0212	0·00615	0·00393	0·00245	0·00216
8	0·0291	0·0267	0·00756	0·00647	0·00284	0·00329

In the light of Acree's work, the fact that k changes with dilution is strong evidence that the reaction in these solvents also is one between ions and molecules jointly.

Summary.

In the hope of tracing some relation between the constitution of a solvent and its effect on the velocity of a particular reaction, the velocity of reaction between sodium β-naphthoxide and methyl, ethyl, and *n*-propyl iodides has been measured at 50·5° in *N*-concentration in methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec.*-, and *tert.*-butyl, *n*-, *iso*-, *sec.*-, and *tert.*-amyl, allyl, and benzyl alcohols, and ethylene glycol.

It has been found that some relation does exist for these reactions and solvents. The velocity in the *n*-, *iso*-, *sec.*-, and *tert.*-series steadily decreases with increasing molecular weight, with the exception of the anomalous behaviour of methyl alcohol, which is a less favourable solvent than ethyl alcohol. For alcohols of a given molecular weight, the order of decreasing activity is *iso*-, *sec.*-, *n*-, *tert.*-, and is independent of the alkyl iodide.

Allyl alcohol does not compare closely with *n*-propyl alcohol, with which it is physically similar; the effect of the unsaturated group is to decrease the velocity. Benzyl alcohol is a more favourable medium than a straight-chain alcohol of the same molecular weight, and the velocity in ethylene glycol is lower than that in ethyl alcohol, showing that the displacement of a hydrogen atom by a hydroxyl group reduces the velocity. The addition of water to ethyl alcohol at first increases the velocity to a maximum at about 80 per cent. of alcohol, and then retards the reaction.

It is suggested that these facts support the idea that a solvent participates in the reaction, and its physical properties have only a subordinate influence.

The order of the activity of the alkyl iodides is only approxim-

ately independent of the solvent, and the relative activities of the iodides are dependent on the solvent.

The ratio of the activity of sodium phenoxide and naphthoxide is independent of the alkyl iodide, but the ratio of naphthoxide to ethoxide is not so independent.

The influence of initial concentration has also been studied in four solvents. In each case there is an increase in velocity with decreasing initial concentration. In the cases of methyl and ethyl alcohols, evidence is adduced which suggests that in these solvents sodium β-naphthoxide undergoes alcoholysis as well as ionisation.

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69 DOCK STREET,
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LIV.—*The Introduction of the Chloromethyl Group into the Aromatic Nucleus.*

By HENRY STEPHEN, WALLACE FRANK SHORT, and GEOFFREY GLADDING.

UP to the present time, it does not appear that any systematic attempt has been made to prepare benzyl chloride and benzyl bromide and their derivatives by direct introduction of chloromethyl and bromomethyl groups, respectively, into the aromatic nucleus.

Grassi-Cristaldi and Maselli (*Gazzetta*, 1898, **28**, ii, 477) were the first to show that the product (which they called chloromethyl alcohol) obtained by the action of hydrogen chloride on paraformaldehyde reacted with benzene in presence of aluminium chloride to yield benzyl chloride and diphenylmethane. Under such conditions, however, traces only of benzyl chloride could have been formed, since it would react very readily with unchanged benzene in presence of aluminium chloride to form diphenylmethane.

In this paper is described the preparation of benzyl chloride and compounds related to it by the direct introduction of the chloromethyl group into an aromatic compound. The method consists of treating an aromatic compound in presence of a

dehydrating agent with the product obtained by the action of hydrogen chloride on paraformaldehyde or aqueous solutions of formaldehyde, which has been shown to consist of *s*-dichloromethyl ether (Tischtschenko, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 464; Lösekann, *Chem. Zeit.*, 1890, **14**, 1408; Litterscheid, *Annalen*, 1901, **316**, 157; Litterscheid and Thimme, *Annalen*, 1904, **334**, 1). If methyl alcohol is present in the commercial formaldehyde employed, a small amount of monochloromethyl ether will also be present (Henry, *Ber.*, 1893, **26**, 933).

Both these compounds yield chloromethyl derivatives when treated with aromatic compounds in the presence of a dehydrating agent, but there is an essential difference between the two cases, for whilst *s*-dichloromethyl ether reacts very readily with benzene in the presence of anhydrous zinc chloride to give benzyl chloride, monochloromethyl ether under similar conditions reacts slowly. If zinc chloride monohydrate is substituted for anhydrous zinc chloride in the latter case, the reaction takes place readily. A possible explanation of these facts is indicated by the following scheme:

(i) $(CH_2Cl)_2O + 2C_6H_6 = 2C_6H_5{\cdot}CH_2Cl + H_2O$.
(ii) $CH_3{\cdot}O{\cdot}CH_2Cl + H_2O = CH_3{\cdot}OH + CH_2Cl{\cdot}OH$.
(iii) $2CH_2Cl{\cdot}OH = (CH_2Cl)_2O + H_2O$.

The formation of benzyl chloride is explained by (i), and the water produced in the reaction would thus be available to bring about the hydrolysis of monochloromethyl ether according to (ii), two molecules of the chloromethyl alcohol thus formed then uniting with elimination of water to produce *s*-dichloromethyl ether. The reactions indicated by (ii) and (iii) explain why the monohydrate of zinc chloride brought about a quicker reaction between benzene and monochloromethyl ether. Furthermore, it has been observed that when monochloromethyl ether (b. p. 59—61°) was treated with the monohydrate of zinc chloride at about 27° and the mixture vigorously agitated, the product was *s*-dichloromethyl ether (b. p. 105—106°). The temperature of 27° is that at which the monohydrate deposits anhydrous zinc chloride.

The formation of a chloromethyl aromatic compound is usually accompanied by the production of a diphenylmethane derivative, which is formed by the condensation of the chloromethyl compound with the original aromatic compound. The latter reaction depends on the kind of dehydrating agent employed, since those reactions in which zinc chloride was used only furnished small amounts of the diphenylmethane derivatives, whereas the use of sulphuric acid under similar conditions invariably caused the formation of larger quantities of those substances. In both instances, however, the

temperature is an important factor, because, as a rule, diphenylmethane derivatives are formed to some extent by heating a mixture of a chloromethyl compound with another aromatic compound; the conditions for this reaction are more favourable when substances such as sulphuric acid, metallic oxides, or even traces of metals like iron, zinc, and mercury are present. Diphenylmethane was formed, for example, by treating benzyl chloride with benzene and concentrated sulphuric acid, and in absence of benzene a substance of complex nature was formed by the reaction of benzyl chloride with itself. Hydrogen chloride was copiously evolved in both reactions. The above statements hold true for other chloromethyl compounds, and as a result of preliminary investigations it was considered advisable to perform the reactions at temperatures not exceeding 35° in most cases, as otherwise the yield of chloromethyl derivative is diminished and the amount of diphenylmethane derivative increased.

For convenience, the various cases investigated which have led to the formation of chloromethyl or bromomethyl derivatives have been tabulated, as follows:

Compound investigated.	Compounds prepared.
Benzene	Benzyl chloride, *ωω′*-dichloro-*p*-xylene, benzyl bromide.
Toluene	*ω*-Chloro-*p*-xylene, *ω*-bromo-*p*-xylene.
Xylene (commercial)	*ω* (1)-Chloro-*ψ*-cumene.
Benzyl chloride	*ωω′*-Dichloro-*p*-xylene.
Benzyl bromide	*ωω′*-Dibromo-*p*-xylene.
Chlorobenzene	*p*-Chlorobenzyl chloride, *p*-chlorobenzyl bromide.
Bromobenzene	*p*-Bromobenzyl chloride, *p*-bromobenzyl bromide.
o-Chlorotoluene	2-*ω* (4)-Dichloro-*p*-xylene.
Nitrobenzene	*m*-Nitrobenzyl chloride.
o-Nitrotoluene	*ω* (4)-Chloro-2-nitro-*p*-xylene.
p-Nitrotoluene	*ω* (2)-Chloro-4-nitro-*o*-xylene.

In addition to the above, other substances have also been investigated, but the results obtained were either unsuccessful or no reaction was observed. Diphenyl, for example, gave *ωω′*-dichloro-*p*-ditolyl, but this we were unable to obtain in a pure condition, the evidence for its formation depending on the fact that the crude product gave diphenyl-4:4′-dicarboxylic acid on oxidation. Naphthalene, when mixed with dichloromethyl ether and allowed to remain at the ordinary temperature for two days, gives a product which resembles that described by Wheeler and Jackson (*J. Amer. Chem. Soc.*, 1902, **24**, 752) from formaldehyde and naphthalene. It possesses remarkable stability towards reagents such as potassium permanganate and chromic acid, and is only slightly attacked by fusion with a mixture of potassium hydroxide and potassium chlorate. Anthracene and anthraquinone were

recovered unchanged from the reaction mixtures, as was also the case with *m*-dinitrobenzene and *s*-trinitrotoluene respectively.

Phenol gave the well-known "bakelite" product, whereas from anisole good yields of *pp'*-dimethoxydiphenylmethane were obtained. The latter substance is also readily obtained by warming anisyl chloride (prepared by treating anisyl alcohol with phosphorus pentachloride in dry ether) with anisole.

In the cases of bases such as aniline, *o*-, *m*-, and *p*-toluidines, the so-called anhydro-bases were obtained. Dimethyl and diethyl aniline readily yield tetramethyl- and tetraethyl-diaminodiphenylmethane respectively. No reaction was observed with *o*- and *p*-chloronitrobenzene, *p*-dichlorobenzene, or *p*-chlorotoluene.

The introduction of a chloro- or bromo-methyl group into monosubstituted benzenoid compounds, such as toluene or chlorobenzene, appears to take place exclusively in the para-position. No evidence was found of the presence of the corresponding ortho-derivatives in the products. Benzyl chloride similarly gave only $\omega\omega'$-dichloro-*p*-xylene.

The presence of a nitro-group directs a chloromethyl group into the meta-position.

EXPERIMENTAL.

The Action of Hydrogen Chloride on Formaldehyde, Paraformaldehyde, and Hexamethylenetetramine.

Formaldehyde.—The apparatus consisted of a tower packed with glass beads, and the lower end was inserted in one neck of a Woulfe's bottle, which was provided with an outlet tap at the bottom. At the top of the tower, a suitable condensing arrangement was attached. Formaldehyde solution (40 per cent.) was allowed to percolate slowly down the tower, and at the same time a rapid stream of hydrogen chloride was passed upwards through the other inlet of the Woulfe's bottle. The reaction soon became evident from the fact that the tower was warm after the first two or three minutes. As the liquid collected in the receiver, the formation of oil was observed almost at once, and as the quantity of liquid increased, the oil was seen floating on the acid layer. The oil sinks only after saturation with hydrogen chloride, and the above method therefore has the advantage of yielding oil containing less hydrogen chloride than is the case in Lösekann's method.

It is important to note that when hydrogen chloride was passed into formaldehyde solution (40 per cent.), and the latter cooled

during the experiment by immersion in cold water, paraformaldehyde separated from the solution. It is difficult to convert paraformaldehyde into oil by this method when formed in such circumstances.

For satisfactory yields of oil, it is essential, therefore, that the heat produced during the reaction between formaldehyde solution and hydrogen chloride should be allowed to develop; the temperature seldom exceeded 60°, and in the tower experiment described above there was no appreciable loss of formaldehyde due to rise in temperature.

Paraformaldehyde.—Thirty grams (1 mol.) of paraformaldehyde were suspended in 40 grams of concentrated sulphuric acid (D 1·73), the mixture was cooled to 0°, and 175 grams (1·5 mols.) of chlorosulphonic acid were slowly added. The reaction is easily controlled by carefully adjusting the flow of chlorosulphonic acid, and the temperature should not be allowed to rise above 10°, otherwise the reaction becomes very violent and much paraformaldehyde is lost as vapour. The yield of *s*-dichloromethyl ether is 95 per cent. of the theoretical (compare *J. Soc. Chem. Ind.*, 1919, **38**, 468R).

Hexamethylenetetramine.—Twenty grams of hexamethylenetetramine were dissolved in 150 c.c. of concentrated hydrochloric acid, the solution was cooled in ice, and a rapid stream of hydrogen chloride was introduced. After ten minutes, a layer of oil was formed on the surface of the liquid, with simultaneous deposition of ammonium chloride. The oil was separated and purified, when it distilled at 105°, and only a small residue was left. The yield of *s*-dichloromethyl ether was about 50 per cent. of the theoretical.

In the experiments to be described later, the oil produced from 40 per cent. formaldehyde solution was employed, as being more economical and readily procurable. The presence of monochloromethyl ether does not affect the formation of chloromethyl derivatives when the oil is condensed with aromatic compounds, since it was found possible to prepare such derivatives from aromatic compounds and monochloromethyl ether. In the subsequent section dealing with the preparation of chloromethyl derivatives, the product from the action of hydrogen chloride on formaldehyde will be referred to as "crude oil." A rapid method for the preparation of small quantities of the "crude oil" consists in gradually adding sodium chloride to a suspension of paraformaldehyde in concentrated sulphuric acid, when the oil separates as an upper layer.

Properties of the Crude Oil.—On shaking the crude oil with sodium silicate, borax, or potassium carbonate, any excess of free hydrogen chloride is removed, the oil being slightly decomposed, with the formation of paraformaldehyde; more decomposition

esults if anhydrous sodium sulphate is used as a dehydrating gent.

The dry oil, from which excess of hydrogen chloride has been emoved, is only slowly attacked by solid sodium or potassium ydroxides; the crude oil before drying is almost completely lestroyed by such treatment.

Both the crude and treated oils are stable towards concentrated sulphuric acid, on which they float. Phosphoric oxide attacks the crude oil very vigorously, with the formation of paraformaldehyde; the oil treated as above is attacked only very slowly by this reagent.

The oil is volatile in a current of steam, about a half of it being destroyed in the process. This fact is of importance in connexion with the isolation of chloromethyl derivatives. These are obtained from the reaction mixtures by distillation in steam, and, in consequence, any unchanged oil is found mixed with such derivatives, and on purification of them by distillation, decomposition results. Unchanged oil may be easily removed by adding a little dilute potassium permanganate to the steam distillate until the colour of the solution is just pink; the oil is readily oxidised, and the odour of formaldehyde, usually present, disappears.

The Action of Hydrogen Bromide on Formaldehyde.

Thirty grams (1 mol.) of paraformaldehyde were suspended in 80 grams of sulphuric acid (D 1·84), the mixture was cooled in ice, and 155 grams (1·5 mols.) of finely powdered sodium bromide were slowly added with constant agitation. Only a small amount of bromine was evolved. The mixture was then warmed on the steam-bath for ten minutes, when the paraformaldehyde rapidly dissolved, and an oily layer of *s*-dibromomethyl ether appeared on the surface of the acid. On distillation of the crude product, about 80 grams of pure *s*-dibromomethyl ether were obtained (b. p. 154—155°). The properties of the oil are similar to those described for the corresponding chloro-compound.

The Preparation of Aromatic Chloromethyl Derivatives. Benzyl Chloride.

As the preparation of benzyl chloride is a typical example of the general mode of procedure, the following remarks are of general interest.

The yield of benzyl chloride is increased if the reaction is carried out at temperatures not exceeding 30°, the best results being obtained at the ordinary temperature. In most cases, it is neces-

sary to cool the reaction vessel with a rapid stream of cold water to avoid rise in temperature, the reaction mixture being well shaken by mechanical means or stirred by means of a rapid rotating Witt's stirrer.

In calculating the quantities of benzene and anhydrous zinc chloride to be used, so much of the latter was taken that if the reaction proceeded to completion, 2 molecules of water would be eliminated, forming zinc chloride dihydrate according to the equation

$$ZnCl_2 + 4C_6H_6 + 2(CH_2Cl)_2O = 4C_6H_5 \cdot CH_2Cl + ZnCl_2,2H_2O.$$

It was found advantageous to use an excess of benzene in the condensation, otherwise unchanged *s*-dichloromethyl ether appeared in the distillate. A mixture of 108 grams of benzene and 68 grams of powdered anhydrous zinc chloride was shaken mechanically, and 79·5 grams of the crude oil added gradually, the temperature being kept below 25°. An immediate red coloration was observed, which became darker on further addition of the oil. When all the oil had been added, the shaking was continued for about an hour to complete the reaction. Ice-water was then added to the product, when the red colour disappeared, and the mixtnre was distilled in a current of steam.

Unchanged benzene distilled over rapidly, accompanied by the odour of formaldehyde, and at this stage the receiver was changed, as it was observed that the oil carried over in the distillate was heavier than water and possessed the characteristic odour of benzyl chloride as well as that of formaldehyde. When nearly the whole of the benzyl chloride had been removed, a white, crystalline mass was observed to solidify in the condenser. The distillation was then stopped, a pale brown oil remaining in the flask. This oily residue partly solidified on cooling, and was preserved, along with the white, crystalline mass mentioned above, for further investigation.

The aqueous suspension of the oil was treated with dilute potassium permanganate until the odour of formaldehyde had disappeared, the oil separated from water after settling, dried with anhydrous sodium sulphate, and distilled, 44 grams of benzyl chloride (b. p. 174°) being obtained.

Better yields were obtained using the entire crude product, that is, both the oil and the concentrated hydrochloric acid layers, together with benzene, and sufficient anhydrous zinc chloride to convert the water present, and that produced during the reaction, into the dihydrate, $ZnCl_2,2H_2O$.

The materials were added in the same order as in the previous

xperiment, the temperature being kept below 10° and the mixture vell shaken throughout.

Using 100 c.c. of formaldehyde (40 per cent.), 104 grams of benzene, and 140 grams of anhydrous zinc chloride, 57 grams of benzyl chloride were obtained. A brown-coloured residue also remained as before in the flask after distillation with steam.

In order to avoid the vigorous agitation required to emulsify the reaction mixture, on which the success of the operation largely depends, attempts were made to attain the same object by the use of finely divided kieselguhr. The results obtained were as follows, in each case 60 grams of crude oil being mixed with 100 grams of benzene and 68 grams of anhydrous zinc chloride.

Experiment.	Yield of benzyl chloride.	Time.
(I.) Kieselguhr ground with $ZnCl_2$	36 grams	1 hour.
(II.) Kieselguhr suspended in $ZnCl_2,H_2O$......	28 ,,	$\frac{3}{4}$,,
(III.) Finely powdered $ZnCl_2$	36 ,,	$2\frac{1}{2}$ hours
(IV.) $ZnCl_2,H_2O$....................................	28 ,,	$1\frac{3}{4}$,,

By comparison of the above experiments, it will be seen that agitation may be avoided by the use of kieselguhr, which also assists in diminishing the time required for the experiment without affecting the yield, and the possibility of formation of by-products was also eliminated. The yield of benzyl chloride is better when anhydrous zinc chloride is used rather than the monohydrated form, but the dehydrating properties of the latter in the presence of concentrated hydrochloric acid are better than the former, as is shown in the second experiment described above.

The dehydrating properties of the monohydrate of zinc chloride are of interest in connexion with the following experiment.

If pure monochloromethyl ether is condensed with benzene in the presence of zinc chloride in the manner above described, the following results are obtained, using 49 grams of benzene and 25 grams of monochloromethyl ether.

(i) Using anhydrous zinc chloride in sufficient quantity to form the monohydrate, 14·5 grams of benzyl chloride were obtained after five hours.

(ii) Using zinc chloride monohydrate in sufficient quantity to form the dihydrate, 14·5 grams of benzyl chloride were obtained after three-quarters of an hour.

These results are explained by the fact that hydrolysis of monochloromethyl ether must occur before the main condensation takes place, as mentioned in the introduction.

Thus, if no water is present in the zinc chloride, the reaction proceeds very slowly, since there is no tendency for the dehydration to take place until partial hydrolysis occurs.

In the case of the crude oil from formaldehyde, this contains much *s*-dichloromethyl ether, which may be condensed without hydrolysis to form benzyl chloride:

$$2C_6H_6 + (CH_2Cl)_2O = 2C_6H_6{\cdot}CH_2Cl + H_2O.$$

The change represented by this equation may be realised in practice by allowing a mixture of benzene and the crude oil to remain for several days. A small quantity of benzyl chloride is obtained, the formation of which is probably facilitated by the presence of hydrogen chloride dissolved in the crude oil.

In the reaction between benzene and *s*-dichloromethyl ether, water should be carefully excluded unless it has been previously saturated with hydrogen chloride, otherwise a considerable amount of hydrolysis of *s*-dichloromethyl ether takes place, according to the equation

$$(CH_2Cl)_2O + H_2O = 2HCl + 2CH_2O,$$

and this accounts for the poorer yields of benzyl chloride obtained if the monohydrate is used as dehydrating agent.

From Paraformaldehyde.—Thirty grams of paraformaldehyde and 127 grams of anhydrous zinc chloride were suspended in 100 grams of benzene, the mixture being cooled in ice and treated with dry hydrogen chloride for several hours. The product was then poured into water, and, on distillation in a current of steam and subsequent purification, 35 grams of benzyl chloride were obtained. A large residue remained in the flask after distillation with steam, the composition of which appeared to be of a very complex nature.

From Hexamethylenetetramine.—Forty grams of hexamethylenetetramine were mixed with 35 grams of powdered zinc chloride and suspended in 54 grams of benzene. Dry hydrogen chloride was passed into the mixture for eight hours, a red coloration being produced, which disappeared on pouring the mixture into water. Only a very small residue was left after distillation with steam, and the distillate, after purification, gave 5 grams of benzyl chloride.

An experiment was carried out with the object of combining the action of hydrogen chloride on formaldehyde with the subsequent one for the formation of benzyl chloride. Benzene (104 grams) was emulsified with formaldehyde solution (100 c.c. of 40 per cent.) by vigorous stirring, using a rapidly rotating Witt's stirrer, hydrogen chloride was passed into the emulsion, which was cooled in ice, and finely powdered zinc chloride (140 grams) added gradually during four hours. The yield of benzyl chloride was 23 grams, and much residue remained after distillation with steam. The disadvantage of this method is that the temperature is very difficult

o control, owing to the heat evolved during the action of hydrogen :hloride on formaldehyde.

A further experiment, carried out without the use of zinc :hloride, gave 10 grams of benzyl chloride, using the same quanti- :ies as before.

As stated previously, the use of sulphuric acid as a dehydrating agent instead of anhydrous zinc chloride in the above reactions gives poorer yields of benzyl chloride. The results obtained from a series of experiments indicate that the more concentrated the acid the smaller is the yield of benzyl chloride, and, in particular, sulphuric acid of concentration higher than 80 per cent. causes decomposition of the benzyl chloride formed during the reaction. On the addition of sulphuric acid (concentration varying from 80 per cent. and higher) to pure benzyl chloride, a copious evolution of hydrogen chloride took place, with the formation of a gum-like residue, which was insoluble in the usual organic solvents. Such a residue was the chief product obtained from the experiments, which also yielded only small amounts of benzyl chloride. In the case of sulphuric acid of concentration less than 80 per cent., the power of dehydration necessary for the reaction had been considerably diminished, and the operation was thus prolonged, a fact which militated against the success of the experiments.

ωω'-Dichloro-p-xylene.—The presence of this substance in the reaction mixture during the preparation of benzyl chloride has already been mentioned, and the amount was observed to increase when the reaction was carried out between 30° and 40°. A mixture of 72 grams of crude oil and 34 grams of finely powdered anhydrous zinc chloride was warmed at 35° for ten hours, during which time 39 grams of benzene were gradually added, the mixture being continually agitated. The latter became intensely red, the colour disappearing on pouring it into water at the end of the prescribed time. After the removal of the benzene and benzyl chloride in a current of steam, the residue was cooled, extracted with ether, the solution dried, and evaporated, when a semi-solid mass remained, which was distilled under diminished pressure, 22 grams of a white solid (b. p. 120°/20 mm., m. p. 97—99°) being obtained. It crystallised from ethyl alcohol in leaves melting at 100·5° (Lauth and Grimaux, *Zeitsch. f. Chem.*, 1867, **3**, 381, give 100°) (Found: Cl=40·28. Calc.: Cl=40·52 per cent.).

ωω'-Dichloro-*p*-xylene (10 grams) was also obtained by warming benzyl chloride (25 grams) and the crude oil with anhydrous zinc chloride at 30—35° for eighteen hours. After purification in the manner previously described, the substance melted at 100·5°. It

is readily soluble in cold chloroform or acetone and in hot ethyl or methyl alcohol, from which it crystallises, but sparingly soluble in ethyl acetate, benzyl chloride, ether, or glacial acetic acid. On warming with water at 80°, it is easily hydrolysed, the presence of free hydrochloric acid being detected in the aqueous portion. On oxidation, the substance gave terephthaldehyde (colourless needles, m. p. 116—117°, Hönig, *Monatsh.*, 1889, **9**, 1153) and terephthalic acid (m. p. 140°), the mononitro-derivative of the latter melting at 259°.

Benzyl Bromide.—This substance was prepared by treating benzene with the crude oil. The method of procedure was similar to that described in the case of benzyl chloride, and the same yields of benzyl bromide were obtained, the product distilling at 114°/15 mm.

*ωω′-Dibromo-*p*-xylene.*—This was isolated from the residue after removing benzyl bromide. After purification in the way already described for the corresponding chloro-compound, it crystallised from ethyl alcohol in glistening leaves melting at 144°, and on oxidation with potassium permanganate it yielded terephthalic acid.

*ω-Chloro-*p*-xylene.*—This was obtained (35 grams) from toluene (55 grams) by the methods previously described for benzyl chloride as a colourless liquid (b. p. 92—94°/20 mm., 192°/760 mm.) (Found: Cl = 23·9. Calc.: Cl = 24·3 per cent.). Its identity was established by the preparation from it of terephthalic acid, *p*-tolualdehyde (b. p. 102—105°/20 mm., 202°/758 mm.; oxime, m. p. 77—78°; *p*-nitrophenylhydrazone, m. p. 192°), and *p*-xylyl alcohol (m. p. 59°; acetate, b. p. 225—227°/758 mm., 121—123°/18 mm.).

*ω-Bromo-*p*-xylene.*—This was prepared by treating toluene with the crude bromo-oil and zinc chloride monohydrate. After purification, it was obtained as a heavy, colourless oil, which solidified after two distillations under diminished pressure (b. p. 109°/15 mm.), and the solid compound melted at 38° (Radziszewski and Wispek, *Ber.*, 1882, **15**, 1743, give 35·5°) (Found: Br = 43·09. Calc.: Br = 43·2 per cent.).

*Di-*p*-tolylmethane.*—This substance was isolated from the brown oil which remained after removing ω-chloro-*p*-xylene in a current of steam. The oil was dissolved in ether, the solution dried, evaporated, and the residue distilled, when a chief fraction consisting of a pale yellow oil passed over at 180°/13 mm. On redistillation under the ordinary pressure, the product was a colourless oil, boiling at 293°, which showed a faint blue fluorescence, and was insoluble in water, but readily soluble in the ordinary organic solvents. On cooling in a mixture of ice and salt, it solidified, and,

after draining the crystals and re-melting them, they showed a setting point of 22·5°. Ador and Rilliet (*Ber.*, 1879, **12**, 2302) give the melting point of di-*p*-tolylmethane as 23°, and Lavaux (*Compt. rend.*, 1911, **152**, 1400) gives 28° (Found: C = 91·55; H = 8·03. Calc.: C = 91·82; H = 8·16 per cent.).

A portion of the substance was nitrated by warming with nitric acid (D 1·42) on the water-bath at 60—70° until the oily layer had disappeared. On pouring into water, a white, crystalline substance separated, which was collected, washed with hot water, and then with sodium carbonate solution, in order to remove a small quantity of an acid formed by oxidation. The product was boiled with water, collected, and dried, and on crystallisation from acetic acid the first crop of crystals (plates) melted at 169—170°. A mixture of it with 3:3′-dinitrodi-*p*-tolylmethane (p. 526) showed no depression of the melting point. The filtrate deposited a further crop of crystals, which were twice recrystallised from acetic acid and then melted at 143—144°, and were identical with 3:3′-dinitro-4:4′-dimethylbenzophenone (p. 526). This substance is more readily soluble in acetic acid than the corresponding diphenylmethane derivative.

4:4′-*Dimethylbenzophenone.*—This was obtained by the oxidation of di-*p*-tolylmethane with chromic acid in acetic acid, the solution being kept cold. After an hour, the mixture was poured into much water, and the precipitate was collected, washed several times with sodium carbonate solution, and then crystallised from ethyl alcohol, from which the ketone separated in needles melting at 98° (Limpricht, *Annalen*, 1900, **312**, 92, gives 95°).

On fusion of the ketone with an excess of potassium hydroxide at 200°, the odour of toluene was observed, and the fused mass, after cooling and acidifying with hydrochloric acid, gave an acid which was crystallised from hot water, in which it was readily soluble, and melted at 177°. It was identified as *p*-toluic acid, and there was no evidence of the presence of *o*-toluic acid, which, however, is only sparingly soluble in hot water.

Prolonged action of chromic acid in acetic acid solution, or oxidation with potassium permanganate, converts di-*p*-tolylmethane into benzophenone-4:4′-dicarboxylic acid crystallising from acetic acid in needles, which sublime on heating (the silver salt gave Ag = 44·4. Calc.: Ag = 44·6 per cent.). The methyl ester melts at 224°, as stated by Limpricht (*loc. cit.*). Fusion of the acid with potassium hydroxide yielded a mixture of terephthalic and benzoic acids, which was easily separated, since the former is only very sparingly soluble in hot water, and the two constituents were identified in the usual way.

ω(1)-*Chloro-ψ-cumene* ($CH_2Cl:Me:Me = 1:3:4$).—It was not possible to study the reactions of the three xylenes individually, as these were not available. The above substance, however, was isolated from the product obtained by treating ordinary xylene with the crude oil, according to the method described in the case of toluene. It distils at 215—216° under the ordinary pressure (105°/15 mm.) (Curtius and Mayer, *J. pr. Chem.*, 1912, [ii], **85**, 143, give 103—104°/19 mm.), and possesses an odour resembling that of benzyl chloride (Found: Cl = 22·5. Calc.: Cl = 22·98 per cent.).

On reduction with red phosphorus and hydriodic acid, it gave ψ-cumene (b. p. 168—169°), the trinitro-derivative of which melted at 185°.

On converting into the aldehyde in the usual way, and subsequent oxidation of the latter, 2:4-dimethylbenzoic acid was obtained (m. p. 125°) (silver salt, found: Ag = 41·87. Calc.: Ag = 42·02 per cent.).

p-*Chlorobenzyl Chloride*.—This substance is readily prepared from chlorobenzene and the crude oil by any of the methods previously described. Good results were obtained by using zinc chloride monohydrate as dehydrating agent and carrying out the experiment at 65°. Employing 97 per cent. sulphuric acid at 25°, 50 per cent. of the chlorobenzene was converted into *p*-chlorobenzyl chloride, but higher temperatures favour the formation of 4:4′-dichlorodiphenylmethane; the yield of the latter is nearly theoretical at about 40°. *p*-Chlorobenzyl chloride was also obtained by treating chlorobenzene with monochloromethyl ether in the presence of dehydratiug agents. It melted at 29° and boiled at 117°/20 mm. and 214°/758 mm. (Found: Cl = 44·48. Calc.: Cl = 44·1 per cent.). In order further to characterise this substance, *p*-chlorobenzoic acid (m. p. 236°), *p*-chlorobenzaldehyde (m. p. 46—47°), and *p*-chlorobenzyl alcohol (m. p. 70—71°) were prepared from it.

4:4′-*Dichlorodiphenylmethane*.—This substance was isolated from the residue after removing *p*-chlorobenzyl chloride in a current of steam. The brown oil was separated from the aqueous layer, dried, and distilled, when 4:4′-dichlorodiphenylmethane passed over as a colourless oil at 208—210°/15 mm., which solidified to a mass of white needles, and after crystallisation from methyl alcohol melted at 55°; this is identical with the value given by Montagne (*Rec. trav. chim.*, 1907, **25**, 390).

The compound was also obtained by treating *p*-chlorobenzyl chloride with chlorobenzene and sulphuric acid.

Five grams (1 mol.) of *p*-chlorobenzyl chloride were melted with 3·5 grams (1 mol.) of chlorobenzene, and, after cooling, the mix-

ture was treated with four times its weight of 97 per cent. sulphuric acid. It was then well shaken until emulsified and hydrogen chloride was evolved. The reaction was moderated by cooling in water, and the mixture was allowed to remain overnight. On passing a current of steam through the semi-solid mass after treatment with water, small amounts of unchanged chlorobenzene and *p*-chlorobenzyl chloride passed over, and 5 grams of 4:4′-dichlorodiphenylmethane were obtained from the residue by the method of purification described above.

4:4′-Dichlorobenzophenone.—This was obtained by treating 4 grams (1 mol.) of 4:4′-dichlorodiphenylmethane dissolved in 20 grams of glacial acetic acid with 4 grams (1 mol.) of chromic acid. The temperature of the solution rapidly rose, and it was necessary to cool the mixture in order to control the vigorous action which took place. After an hour, the dark green solution was poured into 250 c.c. of water, when glistening plates separated which, after crystallisation from ethyl alcohol, melted at 145°. The oxime melted at 136° (Dittrich, *Annalen*, 1891, **264**, 174, gives 135°). On fusing 4:4′-dichlorobenzophenone with potassium hydroxide, the odour of chlorobenzene was observed, and *p*-chlorobenzoic acid (m. p. 236°) was isolated.

4:4′-Dichloro-3:3′-dinitrodiphenylmethane.—Three grams of 4:4′-dichlorodiphenylmethane were dissolved in 20 c.c. of nitric acid (D 1·42) by warming on the water-bath, and the heating was continued for one hour. On pouring into water, a white, crystalline solid was deposited, which was collected, washed with hot water, dried, and crystallised twice from acetic acid, when it melted at 196°. The filtrate from the first crystallisation, on keeping overnight, deposited small, white needles, which melted at 132°, and there was no change in melting point when the substance was mixed with 4:4′-dichloro-3:3′-dinitrobenzophenone, prepared by nitrating 4:4′-dichlorobenzophenone.

The compound melting at 196° was analysed:

0·1205 gave 0·1049 AgCl. Cl=21·53.

$C_{13}H_8O_4N_2Cl_2$ requires Cl=21·71 per cent.

In order to determine the positions of the nitro-groups, the substance was oxidised with chromic acid in acetic acid solution in the usual way. The product crystallised from ethyl alcohol in small, hard needles melting at 132°, and consisted of 4:4′-dichloro-3:3′-dinitrobenzophenone.

The usual methods of carrying out the reactions described in the foregoing experiments have been applied to the preparation of the following compounds.

p-*Bromobenzyl Chloride.*—This was obtained from bromobenzene

and the crude oil in the presence of zinc chloride monohydrate. Forty-five per cent. of the bromobenzene was converted into *p*-bromobenzyl chloride, which, after purification, melted at 40° (Errera, *Gazzetta*, 1898, **18**, 239, gives 38—39°). Oxidation with potassium permanganate gave *p*-bromobenzoic acid (m. p. 251°).

4 : 4′-Dibromodiphenylmethane (m. p. 64°) was also isolated from the above reaction.

p-*Chlorobenzyl bromide*, prepared from chlorobenzene and the corresponding bromo-oil, crystallises from ethyl alcohol in needles melting at 48° (Jackson and Field, *Ber.*, 1878, **11**, 905, give 48·5°). Oxidation with potassium permanganate yielded *p*-chlorobenzoic acid.

p-*Bromobenzyl bromide*, prepared from bromobenzene and the bromo-oil, crystallised from methyl alcohol in needles melting at 60—61°. Oxidation converted it into *p*-bromobenzoic acid.

2-ω(4)-*Dichloro*-p-*xylene* ($CH_3 : Cl : CH_2Cl = 1 : 2 : 4$).—This was prepared from *o*-chlorotoluene and the crude oil by treatment with zinc chloride monohydrate, the mixture being allowed to remain for twenty-four hours. After purification, it was obtained as a colourless oil boiling at 124°/20 mm.

Found: Cl = 40·39.

$C_8H_8Cl_2$ requires Cl = 40·52 per cent.

On oxidation with potassium permanganate, an acid was obtained, the ethyl ester of which (b. p. 149°) gave, on hydrolysis, 2-chloro-*p*-toluic acid (m. p. 195—197°) (Found: Cl = 20·44. Calc.: Cl = 20·8 per cent.). Gentle fusion of this acid with potassium hydroxide furnished 2-hydroxy-*p*-toluic acid (m. p. 204—205°).

m-*Nitrobenzyl Chloride*.—Many experiments were carried out with the object of preparing *m*-nitrobenzyl chloride from nitrobenzene and the crude oil, but only a small amount of the substance was isolated from any single experiment.

The best result was obtained by treating 63 grams of nitrobenzene with 80 c.c. of sulphuric acid (D 1·84) to which were added 10 c.c. of fuming sulphuric acid containing 10 per cent. of sulphur trioxide, adding gradually 45 c.c. of the crude oil, and maintaining the mixture at 50° for three days. The dark olive-green liquid was poured into four times its volumes of water and distilled in a current of steam; 56 grams of nitrobenzene were recovered, and 3 grams of a white substance solidified in the cool part of the condenser. A small amount of a dark brown solid was left in the flask.

The white solid was found to consist of *m*-nitrobenzyl chloride, which crystallised from ethyl alcohol in glistening plates melting

it 44·5°. It was converted by oxidation with potassium permanganate into *m*-nitrobenzoic acid (m. p. 139—140°), the methyl ester of which melted at 77·5°.

m-Nitrobenzyl chloride was also obtained by treating nitrobenzene and monochloromethyl ether in molecular proportions with aluminium chloride. The yield, however, is poor, and 3:3′-dinitrodiphenylmethane is the chief product.

ω(4)-*Chloro-2-nitro-*p*-xylene* ($CH_3:NO_2:CH_2Cl = 1:2:4$).—The action of sulphuric acid containing 10 per cent. of sulphur trioxide on mixtures of *o*-nitrotoluene and the crude oil resulted in the formation of small quantities of this compound. The following method, however, was found to give a satisfactory result.

Twenty grams of the crude oil were mixed with 20 grams of *o*-nitrotoluene, and to the clear solution 25 grams of finely powdered aluminium chloride were added during the course of two hours. The solution became darker, and heat was evolved. After remaining overnight, water was added and the mixture distilled in a current of steam, when a mixture of ω(4)-chloro-2-nitro-*p*-xylene and *o*-nitrotoluene passed over, leaving a brown oil in the flask. The mixture was separated by distilling off the *o*-nitrotoluene under diminished pressure.

ω(4)-*Chloro-2-nitro-*p*-xylene* was also obtained by treating a mixture of *o*-nitrotoluene and chloromethyl ether in molecular proportions with a little more than the theoretical quantity of aluminium chloride, and subsequently purifying by the method already described. There was no unchanged *o*-nitrotoluene, but a considerable amount of the brown oil, mentioned above, remained after distillation with steam.

The substance, after crystallisation from methyl alcohol, melts at 45°. It has a violent action on the skin, and the vapour attacks the eyes and nose. It is readily soluble in benzene, chloroform, acetone, or ethyl alcohol.

Found: Cl = 19·07.

$C_8H_8O_2NCl$ requires Cl = 19·11 per cent.

The position of the chloromethyl group was determined (i) by converting a portion of the material into 2-nitroterephthalic acid by oxidation with potassium permanganate; (ii) reduction with tin and hydrochloric acid, by which treatment the chlorine in the side-chain was replaced by hydrogen and the nitro-group reduced in the usual way, *p*-xylidine (b. p. 218°) being isolated from the mixture. The platinichloride was analysed, and the hydrochloride, acetyl and benzoyl derivatives melted at the same temperatures as are recorded in the literature.

3:3′-*Dinitrodi-*p*-tolylmethane.*—The brown oil mentioned in the

above preparation solidified on cooling in ice, was ground with a little ethyl alcohol, and the latter decanted, the operation being repeated several times in order to remove traces of the chloromethyl compound. It crystallised from acetic acid in thin, glistening plates melting at 170°. It is only sparingly soluble in hot ethyl or methyl alcohol, but very readily soluble in cold acetone. A mixture of this substance with the product obtained by treating *o*-nitrotoluene with formaldehyde solution and sulphuric acid (D.R.-P. 67001), which has been shown (Fischer and Gross, *J. pr. Chem.*, 1910, [ii], **82**, 231) to be 3:3′-dinitrodi-*p*-tolylmethane, melted at 170°.

3:3′-*Dinitro*-4:4′-*dimethylbenzophenone*.—This was obtained by oxidising the preceding compound with chromic acid in acetic acid solution at the ordinary temperature. The ketone was washed with dilute sodium carbonate solution, and it crystallised from acetic acid in yellow needles melting at 144°.

On fusion with potassium hydroxide, it undergoes fission at the carbonyl group, yielding 2-nitro-*p*-toluic acid and *o*-nitrotoluene, which were conveniently isolated as the corresponding oxidation products, nitroterephthalic acid and *o*-nitrobenzoic acid respectively. The corresponding 3:3′-diamino-compound and its diacetyl derivative melted at 172° and 196° respectively, as stated by Lange and Zufall (*Annalen*, 1892, **271**, 6).

ω(2)-*Chloro*-4-*nitro*-o-*xylene* ($CH_3:CH_2Cl:NO_2=1:2:4$).—The most satisfactory method of preparing this substance consisted in treating a mixture of 10 grams of *p*-nitrotoluene and 20 grams of crude oil with 50 grams of fuming sulphuric acid containing 20 per cent. of sulphur trioxide. After remaining overnight, the mixture was treated in the usual way, and ω(2)-chloro-4-nitro-*o*-xylene was finally obtained from methyl-alcoholic solution in needles melting at 50°.

The same substance may be prepared by using any of the methods described for the preparation of ω(4)-chloro-2-nitro-*p*-xylene, although the yields are not correspondingly as good.

Found: Cl=18·99.

$C_8H_8O_2NCl$ requires Cl=19·11 per cent.

ω(2)-*Chloro*-4-*nitro*-o-*xylene* is readily soluble in ethyl alcohol, benzene, or ether, but sparingly so in acetone or light petroleum, and its physiological action is similar to that of ω(4)-chloro-2-nitro-*p*-xylene. On reduction with tin and hydrochloric acid, it gave *o*-4-xylidine (m. p. 49°), which was identified by means of its acetyl derivative (m. p. 99°) and analysis of the platinichloride (Found: Pt=29·88. Calc.: Pt=29·93 per cent.).

On oxidation with potassium permanganate, ω(2)-chloro-4-nitro-

p-xylene is converted into 4-nitrophthalic acid (m. p. 159°), from which 4-nitrophthalanil (m. p. 192°) was prepared.

5:5′-Dinitrodi-*o*-tolylmethane was also isolated in the above reaction. It melted at 153° (Weil, *Ber.*, 1894, **27**, 3314), the corresponding 5:5′-diamino-compound at 99°, and the diacetyl derivative of the latter at 269°.

5:5′-Dinitrobenzophenone-2:2′-dicarboxylic Acid.—This compound was readily obtained by oxidising the corresponding diphenylmethane derivative with chromic acid in acetic acid solution, and subsequently treating the crude benzophenone derivative (which has not yet been isolated in a pure condition) with potassium permanganate. It crystallised from ethyl alcohol in well-defined needles, which did not melt at 300°:

0·2620 gave 0·4796 CO_2 and 0·0568 H_2O. C=49·92; H=2·43.

$C_{15}H_8O_9N_2$ requires C=50·01; H=2·34 per cent.

On fusion with potassium hydroxide, 4-nitrophthalic acid and *p*-nitrobenzoic acid were obtained.

In concluding, we desire to express our thanks to Professor Lapworth and Dr. J. E. Myers for the kind interest they have taken in the research.

THE CHEMICAL DEPARTMENT,
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LV.—*A New Hydrogen Sulphide Generator.*

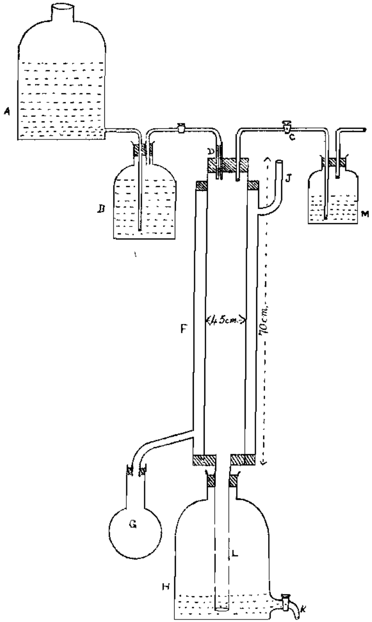
By BERTRAM DILLON STEELE and HENRY GEORGE DENHAM.

THE chief defects common to the usual laboratory forms of hydrogen sulphide generators are to be traced to the comparative slowness of the reaction between acid and sulphide, especially when the concentration of the acid has reached a low value. In consequence of this, a very large apparatus is necessary if it is desired to supply each member of a class with a constant supply of gas, and in order to attain this there is, in general, a great wastage of partly spent acid. In the apparatus herein described, an endeavour has been made to obtain (1) a rapid evolution of gas, and (2) complete neutralisation of the acid.

Preliminary experiments on the effect of temperature on the velocity of the reaction between iron sulphide and hydrochloric acid were carried out in 1911 by Mr. I. Rosenblum at the sugges-

tion of one of the authors, and it was soon established that the two desired objects could be readily attained by bringing about the reaction in the neighbourhood of 100°. The following apparatus was then designed:

A is the acid-holder containing about 15 litres, *B* a smaller



reservoir to retain hydrogen sulphide generated after the tap *C* is turned off, *D* a piece of capillary tubing, 3 cm. long and of 1 mm. bore, inserted to prevent a too rapid outrush of acid when the taps are opened, *F* represents a steam-jacket either of glass or of galvanised iron, *M* a wash-bottle, *H* a reservoir, of 25 litres capacity, to receive the spent acid, and *k* a tap through which the spent

.cid may be readily removed. As a matter of convenience, it is .dvisable to have H sufficiently large to hold the maximum amount .f acid required per demonstration. In order to facilitate the 'isplacement of air from the vessel H by the incoming spent liquor, he tube L has a number of holes blown in it. The steam may be upplied from a 500 c.c. flask, G, and experience has shown that rith a short air-condenser attached to J there is practically com-lete condensation of the escaping steam, so that little or no atten-ion is required.

Mode of Operation.—The apparatus, F, is packed with lumps of ·on sulphide, and the acid-holders are filled with commercial hydro-hloric acid diluted with an equal volume of water. On opening he tap C, acid begins to drip on the sulphide, and, provided steam as been passed through the jacket for a sufficiently long period ɔ ensure thorough heating of the sulphide, each incoming drop of cid reacts with almost explosive violence, and long before the acid as percolated through the heated column it is completely eutralised. In fact, a few pieces of iron sulphide placed in the eceiver H were found to be unacted on after the apparatus had een in constant use for seven months. After generation, the gas asses through the tap C and the wash-bottle M before distribu-on to the students' benches. On turning off either the tap C or he bench taps, the gas generated by the last few drops of acid asses back into the holder B and forces acid into the upper essel A.

General Remarks.—Hydrochloric acid (1 : 1) has been found to be ore suitable than sulphuric acid, owing to the great tendency of rrous sulphate to crystallise out as the spent liquor passes from ıe heated generator into the receiver, thereby causing a block.

The apparatus of the dimensions indicated in the figure is ıfficiently large to supply hydrogen sulphide to the bench of every udent in a class of fifty-four, and will stand all demands made ı it when this class is engaged exclusively on the analysis of mix-ıres containing at least four bases from Groups IIA and IIB, even the extent of enabling them to prepare their own ammonium ılphide. As an example of the economy of the apparatus, a series tests showed that the average consumption of concentrated ydrochloric acid per demonstration of two hours by each student ıgaged as above in Group II analysis amounted to 14 c.c., which as equivalent to 2300 c.c. of hydrogen sulphide at normal pressure ıd the ordinary temperature.

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LVI.—*Direct Experimental Determination of the Concentration of Potassium and Sodium Ions in Soap Solutions and Gels.*

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In a series of papers from this laboratory (McBain, *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **12**, 256; *J. Soc. Chem. Ind.*, 1918, **37**, 249T; McBain and Martin, T., 1914, **105**, 957; McBain and Salmon, *Proc. Roy. Soc.*, 1920, [*A*], **97**, 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426; McBain, Laing, and Titley, T., 1919, **115**, 1279), a theory of soap solutions has been developed which quantitatively correlates their high conductivity, moderate osmotic activity, and colloidal properties. Soaps are conceived as a type of a large class of substances, defined as colloidal electrolytes, which owe their properties to the presence of a heavily hydrated, highly charged, excellently conducting ionic micelle.

Hitherto, in the few cases where colloidal ions were envisaged, kataphoresis was confounded with conductivity, and to such colloidal ions was then ascribed a low mobility, such as that to be expected from a complex ion, or it is a well-known and striking fact that the kataphoresis of colloidal particles, and even of coarse suspensions, is in general almost comparable in velocity with the movement of a slow ion. Moreover, it was only in the few cases referred to that kataphoresis was interpreted as conductivity.

The carefully substantiated data for soap solutions obtained by several independent and corroboratory methods force us to ascribe to the ionic micelle an equivalent conductivity which is even greater than the sum total of the conductivities of the ions from which it is derived. This is explained on mechanical grounds, making use of the principle of Stokes's law by conceiving the ionic micelle as an aggregation of fatty ions, such as palmitate ions, which have retained their electrical charges. The ionic micelle must include also, and is probably stabilised by, a large amount of neutral colloid and of hydrate water.

It is clear that the ionic micelle must possess high electrical mobility, but very low mechanical mobility. Under the influence of electrical forces, the mobility of the micelle is magnified in direct proportion to the number of ionic charges which it comprises, whereas for purposes of diffusion the driving force is only that of an individual ion.

The object of the present investigation was twofold: first, to

t as directly as possible the quantitative data already deduced our theory by a further independent method, and, secondly, to nonstrate this distinction between electrical and mechanical bility. The method employed was that of electromotive force, ing potassium and sodium electrodes. The results are as good quantitative confirmation as could be expected. The solutions tually studied were potassium laurate at room temperare, since it is the highest soap which gives a clear solution at e ordinary temperature and yet shows all the characteristics of higher saturated soap, potassium and sodium oleates at the dinary temperature, and sodium palmitate at 90°, since it has een in other respects the most carefully investigated soap.

EXPERIMENTAL.

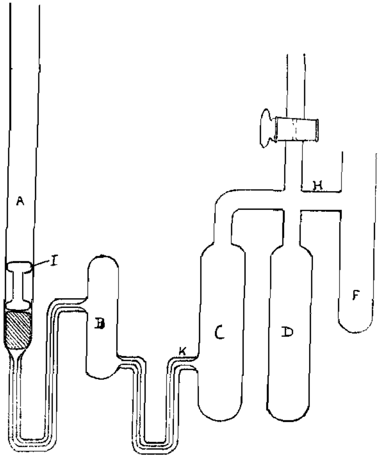
The fatty acids used and the precautions taken in the preparaion of the soap solutions were similar to those described in previous ommunications.

The amalgam for these experiments was prepared in a pure tate by filtering potassium free from oxide through a capillary ube in an inert atmosphere, and distilling mercury into the pure netal so obtained. The apparatus used for the purpose (Fig. 1) is a modified form of that employed by Lewis and Krauss (*J. Amer. Chem. Soc.*, 1910, **32**, 1959; Lewis and Keyes, *ibid.*, 1912, **34**, 119), who were the first to measure the potentials of both sodium and potassium electrodes. The bulb *D* contains mercury previously purified by washing with mercurous nitrate and distillation in a current of air. The apparatus is washed out with dry ammonia gas, and, while the gas is still streaming through, a clean bulb of potassium is introduced into the tube *A* and another into *F*. *A* and *F* are then sealed, and the apparatus is exhausted. The object of the potassium at *F* is to remove all remaining oxygen or water vapour. This is ensured by melting the metal and constantly renewing the surface by tapping the tube until a surface is obtained which remains untarnished. *F* is then removed by sealing at *H*. The apparatus is heated to 120°, the potassium in *A* melts, and is forced by the glass weight *I* through the capillary tube into the bulb *B*, which acts as a trap for any oxide that may have been carried along with the metal. Tubes *A* and *B* are removed by sealing at *K*, and the mercury in *D* is distilled into *C* by raising the temperature to 250°. The resulting amalgam is thoroughly mixed by shaking, and may be kept unchanged for long periods.

Fig. 2 shows the type of electrode used. *A* is a reservoir for

the amalgam, and is connected to the electrode chamber *I* by a two-way stopcock and capillary tube, *B*. (The two-way cock serves to facilitate cleaning the capillary between measurements.) Electrical contact is made by sealing a platinum wire through the capillary tube at *E*. The reservoir is filled by sealing the electrode vessel at *C* to the apparatus in which the amalgam is prepared, washing out with ammonia gas, exhausting, and then opening the stopcock of the amalgam vessel. After filling, the electrode vessel

FIG. 1.



Apparatus for the preparation of clean potassium amalgam.

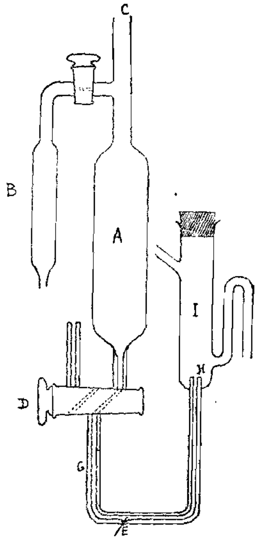
is sealed off at *C*. The calcium chloride tube serves to admit dry ammonia gas to displace the amalgam as it is used.

The solution to be investigated is placed in the electrode chamber, *I*, and amalgam admitted to the capillary tube until a small drop forms at *H*. At first this reacts slightly with the water, and the surface becomes contaminated with hydrogen, but it was found that by renewing the drop once or twice, surfaces could be obtained which remained clear for from ten to twenty

utes. During this period the electromotive force remains stant, but then commences to fall off rapidly. On renewing surface, however, the *E.M.F.* returns to its original value.

'he *E.M.F.* was measured by the potentiometer method, using carefully calibrated resistance boxes (both of 111,110 ohms

Fig. 2.



Electrode for potassium amalgam.

total resistance) instead of a bridge wire. By keeping the total resistance in the two boxes 111,110 ohms and varying the ratio between them, measurements could be made to within less than one-tenth millivolt.

The electrode potentials were measured against the *N*-calomel electrode, using 0·2*N*-potassium chloride as intermediate liquid in

most cases. The cell measured was then of the following type, the arrow showing the direction of the current in the cell:

$$\text{K amalgam} \mid N\text{-K laurate} \mid 0{\cdot}2N\text{-KCl} \mid N\text{-KCl,HgCl} \mid \text{Hg}.$$

(→ under "laurate | 0·2N")

(a) *Potassium Laurate at* 25° *as compared with Potassium Chloride.*

Table I gives the results obtained with three concentrations.

The values in columns in *A*, *B*, *C* represent three different series of measurements carried out with different specimens of amalgam and of potassium laurate, and against a different normal electrode. The agreement between these series is sufficiently good for our purpose, which is to ascertain the concentration of potassium ions in soap solutions by direct comparison with known solutions of potassium chloride.

TABLE I.

Electrode solution.	Middle liquid.	*E.M.F.* (Volts.) *A*.	*B*.	*C*.
N-K laurate	0·2*N*-KCl.	2·183	2·197	2·219
0·5*N*- „	„	2·196	—	2·233
0·2*N*- „	„	2·205	—	2·245
0·5*N*-KCl	„	2·159	2·176	2·196
0·2*N*- „	„	2·182	2·199	2·219

TABLE II.

Potassium Laurate with Different Concentrations of Potassium Chloride as Middle Liquid.

Electrode solution.	*E.M.F.* (Volts.) 0·2*N*-KCl.	0·05*N*-KCl.	0·01*N*-KCl.
N-K laurate	2·219	2·235	2·253
0·5*N*- „	2·233	2·241	2·263
0·2*N*- „	2·245	2·252	2·264

TABLE III.

Potassium Laurate with Different Concentrations of Sodium Chloride as Middle Liquid.

Middle liquid.	*E* calc.	*E* found.
0·2*N*-NaCl	2·244	2·241
0·05*N*- „	2·255	2·254
0·01*N*- „	2·268	2·268

(b) *Potassium Oleate at* 18°.

Potassium laurate had been chosen for investigation as being the highest member in the saturated fatty acid series which could be studied at the ordinary temperature. Potassium oleate, the salt of an unsaturated fatty acid of higher molecular weight, is more colloidal in its behaviour, and its colloidal properties persist in greater dilution than the laurate, whilst its solutions of moderate concentration are quite clear liquids. The highest concentration ($0·6N$), which gave a clear solution, was therefore measured for comparison with potassium laurate. Determinations carried out with three different concentrations of potassium chloride as middle section are given in table IV.

TABLE IV.

	0·1*N*-KCl.	0·05*N*-KCl.	0·01*N*-KCl.
0·6*N*-K oleate......	2·239 volts.	2·245 volts.	2·276 volts.

(c) *Sodium Palmitate at* 90°.

The results obtained for potassium laurate and potassium oleate at the ordinary temperature confirm the hypothesis of an ionic micelle for these solutions, but since a great part of the existing data for soap solutions was obtained at 90°, it was considered desirable to obtain at least one measurement at that temperature with the sodium electrode. The experimental difficulty in working at this temperature lies in the fact that it is difficult to obtain an amalgam which will not react with water. It was found, however, that it was just possible to obtain measurements which, although not very accurate, are yet sufficiently trustworthy to obtain at least a quantitative measurement. A *N*-solution of sodium palmitate was selected for this measurement, since it is one of the most typical soap solutions and the most carefully investigated.

The amalgam was prepared in exactly the same way as potassium amalgam. In carrying out the experiment, two middle sections were used of the same concentration of potassium chloride, one at 90° and the other (communicating with the calomel electrode) at the ordinary temperature, thus keeping the temperature gradient in potassium chloride. Connexion between the soap and the potassium chloride was made by means of a fine capillary tube full of the latter. Table V contains the results for three different middle sections.

TABLE V.

	$0\cdot 1N$-KCl.	$0\cdot 05N$-KCl.	$0\cdot 01N$-KCl.
N-Na palmitate...	2·263 volts.	2·272 volts.	2·295 volts.

The electrode potentials of $N/2$- and $N/5$-sodium chloride were also measured with $0\cdot 1N$-potassium chloride as middle section. They were found to be 2·237 and 2·261 volts respectively.

(d) *Sodium Oleate as Sol and as Gel at* 18°.

A $0\cdot 6N$-solution of this soap was investigated, since it can be obtained at the ordinary temperature in three states, namely, as viscous sol, a clear, transparent gel, and white, opaque curd.

Measurements were carried out at 18° with the sol and gel by the method already described, but it was found impossible to obtain trustworthy results with the curd. Figures for the sol and gel are given in table VI.

TABLE VI.

Middle liquid.	Sol.	Gel.
$N/5$-NaCl	2·284	2·283
$N/10$-NaCl	2·295	2·293
$N/100$-NaCl	2·315	2·314

It will be seen from the above table that the concentration of the sodium ion is the same in the sol and gel. This will be discussed in another paper by Miss M. E. Laing. It is sufficient to say here that the calculated values of V_1, E, and C_1 (see below) are 1·0 mhos., 21 millivolts, and 0·11 normal. The *E.M.F. corrected for diffusion potential, thus becomes 2·263 volts; that* of $N/5$-sodium chloride is 2·254. From these values we obtain a concentration of sodium ions of $0\cdot 11N$, which agrees with that required by the data of McBain, Laing, and Titley. Moreover it should be noticed that the diffusion potential is not affected by the gelation of the sodium oleate.

The Calculation of Diffusion Potential for the Case of an Electrolytic Colloid.

In the introduction above it was made clear that, except where an electrical field of force is the driving agent, it is the mechanical, and not the electrical, mobility of the ionic micelle that will be in evidence. The diffusion potential will therefore depend on the mechanical diffusion velocity of the *ionic micelle*, taken in con-

unction with that of the other ions present, for which, of course, nechanical and electrical diffusion velocity are identical.

Before calculating the concentration of potassium ion from the neasurements given, it is therefore necessary to evaluate the quid potential between such solutions as potassium laurate and otassium chloride. This is by no means negligible, since the rate f diffusion of the potassium ion is many times that of the laurate on or micelle.

It was finally determined in the following manner. The Ienderson formula for a liquid potential gives

$$E = \frac{RT}{F} \cdot \frac{C_1(U_1 - V_1) - C_2(U_2 - V_2)}{C_1(U_1 + V_1) - C_2(U_2 + V_2)}, \ln \frac{C_1(U_1 + V_1)}{C_2(U_2 + V_2)},$$

vhere, in the case under consideration, the concentration, C_1, and he mobilities, U_1 and V_1, refer to potassium laurate, and C_2, U_2, nd V_2 to potassium chloride.

V_1 must be the effective diffusion velocity of the ionic micelle, ogether with that of any laurate ions present. It is not easy to alculate this resultant with any accuracy from previously available data, but if we consider the above equation, there are only hree unknown quantities, C_1, the concentration of potassium ion n soap solutions, V_1, and E, the diffusion potential itself. It is nly necessary to obtain three equations connecting these quantities in order to evaluate them. This can be done by using different oncentrations of potassium chloride as middle section, data for vhich were given in table II. The values for C_1, E, and V_1, calculated from these figures, are shown in table VII.

TABLE VII.

Solution.	V_1 (mhos).	E (millivolts).	C_1 (normality).
N-K laurate	14	17	0·33
·5N- ,, ...	18	13	0·16
·2N- ,, ...	25	7	0·082

It is at once seen that V_1 increases with increasing dilution. This is in accordance with theory, since we know that the relative mount of soap present as crystalloid is greater in dilute solutions han in more concentrated ones. In other words, the more rapidly liffusing laurate ion is being displaced by the more slowly liffusing micelle,* and in the most dilute solution, V_1, approaches he mobility of the former.

* This is, of course, in the opposite direction to the effect of dilution on onductivity, where the displacement of the micelle by ion decreases the nobility.

The values of the diffusion potential are quite large and affect the concentration value of the potassium ion by comparison with the potassium chloride so much that it was considered necessary to test the applicability of the Henderson formula to the present case before accepting these results, especially in view of the fact that we are giving to V_1 a meaning different from that usually given to it. Measurements were therefore carried out, using sodium chloride as middle section. The results of these determinations were given in table III, where, under the column E calc., were given the *E.M.F.'s* of the cell calculated from the value of C_1 and V_1 obtained above. E found contains the experimentally determined values.

The agreement between the calculated and experimentally determined values is quite satisfactory, and we are therefore justified in accepting these values of the diffusion potential so determined as being trustworthy. It will be noted that the diffusibility, V_1, is by no means equal to zero, even for concentrated solutions where the ionic micelle has almost completely displaced the simple fatty ion. It is, indeed, quite a large fraction of the value 20·7, which one expects for a simple fatty ion containing from twelve to eighteen carbon atoms. The explanation is to be sought in the dissociation of soap and micelle that takes place when it diffuses into aqueous potassium chloride, which previously contained no soap. It is proposed to calculate these values later, when the equilibria in soap solutions containing admixtures of chlorides have been sufficiently investigated. It may be pointed out that the concentrations dealt with in the present paper are such that salting out does not occur at the boundaries of salt and soap solutions.

It is now possible to introduce the corrected diffusion potentials in the measurements which McBain and Martin carried out on the hydrogen potential of soap solutions. This affects chiefly the more concentrated solutions, and the result is a diminution in the concentration of the alkali formed on hydrolysis, which still further emphasises its negligible character in concentrated soap solutions. The corrected results will be included in another communication from this laboratory.

Discussion of Results.

I. *Potassium Laurate.* (a) *Concentration of the Potassium Ion.*

The concentration of the potassium ion has already been obtained in the solution of the Henderson formula, but it can be calculated in another manner by comparing the *E.M.F.*, corrected

this diffusion potential, with that obtained for potassium oride. These values are given in table VIII.

TABLE VIII.

Solution.	Corrected $E.M.F.$	Normality of $K^{\cdot}$.
N-K laurate	2·202	0·33
0·5N- "	2·218	0·17
0·2N- "	2·238	0·082
(0·2N-KCl)	(2·210)	(0·167)

The concentrations measured in this manner agree closely with ose tabulated in table VII.

(b) *Comparison with Conductivity and Osmotic Data.*

McBain, Laing, and Titley (*loc. cit.*) have calculated the con- ntration of potassium ion in solutions of potassium laurate, from nductivity data, making the assumption that the laurate micelle as the same electrical mobility as the potassium ion. These alues are included in table IX for comparison with those recorded bove, together with the total concentration of crystalloid present alculated from osmotic data.

TABLE IX.

Solution.	Concentration of $K^{\cdot}$ by $E.M.F.$	Concentration of $K^{\cdot}$ by conductivity.	*Concentration of* crystalloid by osmotic data.
N-K-laurate	0·33N	0·36N	0·40N
0·5N- "	0·17N	0·176N	0·20N
0·2N- "	0·082N	0·065N	0·136N

The agreement between columns two and three is sufficiently close to afford confirmation of the existence of the ionic micelle and to justify the assumption made as to its mobility. For the most concentrated solutions, the conductivity value is higher than that calculated from electromotive force data. To bring these two values into agreement, it would be necessary to ascribe to the micelle a still greater mobility; but it is doubtful if we are justified in doing so, since, in general, conductivity and osmotic data do not closely agree.

In the lowest concentration the conductivity value is low, and the difference between it and the $E.M.F.$ value is undoubtedly real. This is explained by the substitution of the laurate ion for the micelle, and consequent decrease in electrical mobility. In this solution, the concentration of colloid present as micelle is 0·038N, and of the laurate ion 0·044N. If we calculate an average

value for the combined mobility of the micelle and ion from the relation $V = aVm + (1-a)V_2$, where a is the proportion of soap as micelle and $(1-a)$ is the proportion as ion, and Vm and V_2 are the respective mobilities of the micelle and ion, we obtain 40·9 as the combined mobility. Substituting this value in the conductivity calculation, we find $a = \frac{41 \cdot 7}{105 \cdot 6}$. This gives the concentration of potassium ion as $0 \cdot 078N$, which is in much closer agreement with the electromotive force value.

In N-potassium laurate, the concentration of the total crystalloid is $0 \cdot 4N$, and that of the potassium ion 0·33, leaving only 0·07 for all other crystalloid, including undissociated potassium laurate, laurate ion, and hydroxyl ion.

In $0 \cdot 2N$-potassium laurate, the concentration of crystalloid, other than $K^{\cdot}$, is $0 \cdot 054N$, relatively a much greater quantity. This transition from colloid to crystalloid with increasing dilution is quite gradual and regular.

(c) *The composition of the Ionic Micelle.*

We are now in a position to calculate the approximate concentration of all the constituents of potassium laurate solutions. These are given in table X, all concentrations being expressed in mols. per 1000 grams of water.

TABLE X.

Solution.	$K^{\cdot}$.	L'.	KL.	Micelle $(L')_n$.	Neutral colloid $(KL)_m$.
N-K-laurate	0·33	0·04	0·03	0·29	0·64
$0 \cdot 5N$- ,,	0·17	0·02	0·01	0·15	0·32
$0 \cdot 2N$- ,,	0·082	0·044	0·01	0·038	0·04

It is not yet possible to determine with certainty whether the formula of the micelle is $(L')_n(H_2O)_x$ or $(KL)_n(L')_m(H_2O)_x$. We consider it most probable that part of the neutral colloid is absorbed in the micelle. The formula, calculated on the assumption that the whole is taken up, would be $[(KL_{2 \cdot 2})(L')H_2O_x]_m$.

II. *Potassium Oleate.*

The values for V_1, E_1, and C_1, calculated from the data of table IV, are 12 mhos., 22 millivolts, and $0 \cdot 19N$ respectively. The corrected *E.M.F.* becomes 2·217, and comparing this value with the corresponding *E.M.F.* for $0 \cdot 2N$-potassium chloride, which is 2·219 volts, we obtain $0 \cdot 185N$ for the concentration of the potassium ion in $0 \cdot 6N$-potassium oleate.

The value of V_1 is considerably lower than that for the corresponding concentration of laurate; this would be expected, on account of the higher molecular weight of oleic acid.

The concentration of K˙ deduced by McBain, Laing, and Titley from conductivity and freezing-point data was 0·17*N*, and the total concentration of crystalloid 0·19*N*.

The following table contains the concentrations of all the constituents of this solution.

TABLE XI.

K˙.	Oleate′.	K oleate.	Micelle.	Neutral colloid.
0·185	(0·003)	(0·002)	0·185	0·415

There is thus considerably more colloid present in potassium oleate than in a corresponding concentration of potassium laurate, the amount of soap present as crystalloid in the former being practically negligible. However, the sodium oleate contains even more neutral colloid than the potassium oleate, and only two-thirds as much micelle and alkali ion.

III. *Sodium Palmitate at* 90°.

The values of V_1, C_1, and E work out at 29 mhos., 0·41*N*, and 29 millivolts respectively. The corrected electromotive force becomes 2·234 volts, and comparing this with the *E.M.F.* for 0·2*N*-sodium chloride (2·261 volts), we obtain a concentration of sodium ion of 0·40*N*.

The total concentration of crystalloid from osmotic data was 0·52*N*, and the concentration of Na˙ from conductivity 0·37*N*. From these figures we obtain the following concentrations of all the constituents of *N*-sodium palmitate.

TABLE XII.

Crystalloid.			Colloid.	
Na˙.	Palmitate′.	Na palmitate.	Micelle.	Neutral colloid.
0·40*N*	0·07*N*	0·05*N*	0·33*N*	0·55*N*

The formula of the palmitate micelle, assuming that the whole of the neutral colloid is absorbed into the micelle, would be $[(NaP)_{1\cdot7}(P')(H_2O)x]_n$.

The concentration of sodium ion found from conductivity data was originally calculated by assuming the ionic mobility of the micelle to be equal to that of the acetate ion. Now this is not the true mobility of the micelle, but is an average value, made up

of the mobility of the micelle and of the ion. We can, however, calculate the true mobility of the micelle, using the relative concentrations of micelle and ion recorded above. We then find the mobility of the micelle to be 139, which is the same as the mobility of the sodium ion.

Conclusion.

The results of these electromotive force determinations, both from direction and magnitude of the diffusion potential between soap and potassium chloride, as here interpreted (which could be explained in no other way), and further by comparison with known concentration of potassium and sodium chlorides, supports the theory of colloidal electrolytes advanced from this laboratory.

The concentrations of sodium and potassium ions already deduced from a comparison of conductivity data and osmotic activity are confirmed by the direct measurements here presented for a selection of typical cases at 18° and 90°. Gelation (not formation of white curd) of sodium oleate does not influence the results obtained.

I wish to acknowledge grants from the Research Fund of the Chemical Society and from the Colston Society of the University of Bristol, which rendered it possible to carry out this work, which was commenced in 1914.

My thanks are also due to Prof. J. W. McBain for the constant interest he has taken in my work.

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LVII.—*Studies in Emulsions. Part I. A New Method of Determining the Inversion of Phases.*

By SHANTI SWARUPA BHATNAGAR.

THERE are two methods generally in use of determining whether a given emulsion is one of "oil in water" or "water in oil," namely, the colour-indicator method due to Robertson, and the "drop-method" due to Briggs. The former has been found unsatisfactory by Newman (*J. Physical Chem.*, 1914, **18**, 34), and it is also likely that the character and stability of an emulsion might be disturbed by the introduction into the system of an

organic substance like Sudan III, which is used in this method to colour the oil phase.

Further support for this conclusion is derived from the observation of Clowes (*J. Physical Chem.*, 1916, **20**, 445), who finds that organic substances have a very great effect on the size of globules in emulsions. The "drop-method" suffers a disadvantage on account of the fact that a single drop of an emulsion may not always represent the emulsion, whilst if a representative portion of an emulsion is shaken with a large quantity of oil or water, the temporary emulsion due to mechanical shaking may make it extremely difficult to determine the type.

It is sometimes necessary to determine the critical point when one type of emulsion changes into the other. Besides the defects pointed out above, these methods completely fail to give a sharp indication of the critical point, and are therefore not quite convenient for studying the effects of electrolytes and other substances on emulsions. The method which is now described is free from these defects and indicates the critical point very sharply, and is therefore very useful for studying the changes in the inversion point of emulsions by electrolytes and other chemical agents. Besides being a general method, it is found, as shown further, to facilitate the study of de-emulsification and temporary emulsions. The emulsions can be tested by this method as a whole without treating separate portions by frequent removals of samples.

The Method.

The principle of the method is based on the fact that an emulsion of the oil-in-water type, especially when electrolytes are present, would have a much greater electrical conductivity than the other type when oil, an insulating medium, becomes the continuous phase. Preliminary trials of this method were made with emulsions of olive oil (containing 0·5 per cent. of free oleic acid) and dilute aqueous potassium hydroxide solution, and the emulsions so formed were found to be distinctly of two types, one showing marked conductivity and the other very little. In a set of experiments in which the oil was gradually added to the aqueous phase, it was found, as indicated in tables I and II, that the conductivity decreased in a regular manner according to the amount of oil added until a point was reached when any further addition of oil produced a sudden rapid rise in the resistance of the emulsion. This point must be the critical point. A sensitive milliammeter was used to obtain a sharp indication of this point. Results obtained by this method were checked from time to time

by observations under the microscope, and were found to be invariably correct. Some trials were also made on technical emulsions like margarine, and it was found that most of the samples examined showed very little conductivity. The distinct conductivity exhibited by some samples must be attributed to the fact that complete inversion had not taken place in these emulsions.

EXPERIMENTAL.

The emulsions were prepared in wide-mouthed bottles carefully cleaned with hot chromic acid and boiling water. One set of experiments was tried in which the aqueous phase was gradually added to the oil, and the other in which the oil was gradually added to the aqueous phase. Different strengths of different alkali hydroxides were tried. The bottles were shaken for a constant time after each addition in a powerful mechanical shaker, and the total time of shaking was also kept constant to ensure identical conditions. Most of the experiments of Briggs, Robertson, Newman (*loc. cit.*), Donnan (*Zeitsch. physikal. Chem.*, 1897, **31**, 42), and Clowes (*loc. cit.*) were repeated and their results examined by this method.

The procedure was as follows. The emulsions in the bottle, after suitable shaking, were examined by inserting two clean platinum electrodes fixed at a constant distance, and a constant voltage was allowed to operate for a moment to see whether the needle of the ammeter showed that the emulsion was conducting. If it showed good conductivity, the emulsion was considered of the oil-in-water type; if not, of the reverse type. In order to examine emulsions in small quantities, or a particular portion or sample of emulsion, the bottle was replaced by a clean T-shaped glass container in which two platinum wires were sealed.

Results.

Newman's work throws doubt on the question of inversion by mere dilution, as he was not able to prepare an emulsion of the water-in-oil type with sodium hydroxide and olive oil. Robertson and others claim to have obtained both types. Since Newman's objection to Robertson's emulsion of the water-in-oil type is based on the argument that the colour-indicator method is defective, some tests were made by the electrical method to decide whether both types of emulsions can be formed by sodium hydroxide or sodium oleate and olive oil. The results are indicated in the tables.

TABLE I.

0·933N/100-Potassium hydroxide: 25 c.c. used in each experiment.

Olive oil containing 0·5 per cent. of oleic acid.

Time for shaking, five minutes after each addition.

Electrodes fixed, constant voltage.

Olive oil.	Readings of ammeter.	Types.
5	13·0	Oil in water (creams).
10	12·7	,, ,,
15	12·5	,,
20	12·35	,,
25	11·85	,,
30	11·45	,,
50	10·65	,,
65	10·4	,,
80	10·0	,,
85	0·1	Water in oil (thick) ←
90	—	Jelly-like.
100	—	,,

TABLE II.

Potassium hydroxide as in table I.

Paraffin oil (B.P.) containing 0·5 per cent. of oleic acid.

Other *conditions the same as before.*

Oil.	Readings on ammeter.	Type.
5	13·2	Oil in water.
10	13·0	,,
15	12·7	,,
20	12·8	,,
25	12·6	,,
30	12·3	,,
35	12·0	,,
37	11·8	,,
40	11·7	,,
45	11·3	,,
46	0·1	Water in oil. ←

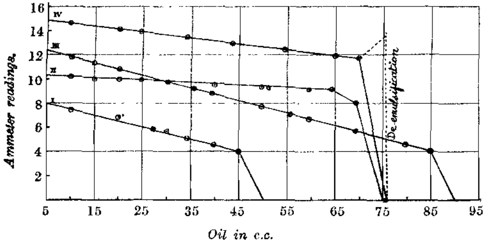
Thus the electrical method shows that by increasing additions of oil to the alkali, a point (indicated by the arrow) is reached when the type changes, as is made evident by the sudden fall in the conductivity of the emulsion to practically zero. These falls are entirely different in their abruptness and suddenness from the fall due to the formation of emulsion or to the action of the alkali on the oil. The graphs represent the changes going on before and at the time of inversion. It is found that the water-in-oil type with kerosene oil is very unstable. The emulsion shows no conductivity for a minute or two, and then it gradually rises

X*

until it indicates its previous conductivity. The drops of water, as they de-emulsify, are visible, and are seen to be constantly falling to the bottom, until the emulsion undergoes complete disintegration.

Effects of Bivalent Alkalis.

Some experiments were tried in which solutions of barium and calcium hydroxides were used instead of sodium and potassium hydroxides. The results were very nearly the same as with univalent alkalis up to a certain concentration (about $N/500$), and the formation of the type appeared to depend only on the ratio of the two phases. As the concentration was increased, however,



I. 5 c.c. of 0·1866 N-potassium hydroxide and paraffin oil (B.P.)
II. 25 ,, 0·000933 N-potassium hydroxide and olive oil.
III. 10 ,, 0·01866 N-potassium hydroxide and olive oil.
IV. 25 ,, 0·000933 N-potassium hydroxide and kerosene oil.

Oleic acid in each case, 0·5 per cent.

it was found that the bivalent alkalis promoted the formation of the water-in-oil type of emulsion, and univalent alkalis that of the reverse type, that is, in concentrations greater than $N/500$ the electrolytic effect predominates over the volume–ratio effect of the two phases. These effects are dealt with more quantitatively later on.

The Zone of Instability.

It was found that the inversion point could be reached from both ends. The critical point was, however, reached in a curious fashion when small amounts of the aqueous solution were added to large quantities of oil. A zone of instability made its appearance, when the emulsion separated into three layers—the top one

ıowing no conductivity, the middle one showing slight conuctivity, and the lower portion high conductivity. This zone of nstability does not appear when the critical point is reached by dding oil gradually in instalments to large quantities of the queous phase.

The probable cause is that when there is present a large quantity of oil containing oleic acid, and the alkali is added in small quantities, the soap formed at the surface between the oil and aqueous solution covers the surface with a thick membrane. This does not dissolve completely in the small amount of water which is present. The surface ceases to be readily mobile, and the spreading out is retarded. Any further additions of the aqueous phase simply settle down under the action of gravity until a sufficient amount of water is accumulated to dissolve the soap membrane. The emulsion, when now shaken, does not divide into three layers. This explanation is further supported by the fact that if the additions of the aqueous phase are large enough, the zone of instability does not seem to make its appearance. Quincke also found that when much alkali is added to a little oleic acid there are obtained oleates more readily soluble in water than when small amounts of alkali are used with much oleic acid.

Stability and Closest Packing.

Walter Ostwald's theoretical considerations on the volumes of the phase ratio at the critical point have been considered to be faulty, as Pickering (T., 1907, **91**, 2001) has been able to obtain emulsions of 99 per cent. of oil and 1 per cent. of water in which oil exists as drops and water as the continuous medium, yet Pickering himself notes that the phase ratios are in most cases in accordance with Walter Ostwald's views of closest packing, and he considers the volume percentage of 74·04 per cent. to be of special significance. Hatschek (*Rep. Brit. Assoc.*, 1918) also notes that all emulsions which separate on standing and have a thin, watery residue yield a stable cream in which oil and water are in the ratio of closest packing, and draws the conclusion that "stability is not complete unless the volume ratios approach the figure corresponding to closest packing."

Robertson was able to emulsify 91·74 per cent. olive oil in 9·26 per cent. alkali, but the strength of the latter was almost 5*N*. He observed that with decreasing strength of alkali, the critical points were shifted near to the point of closest packing. If he had tried still weaker alkalis and stabilised his emulsion by following the precautions suggested by Donnan, and by adding

the phases in small instalments as advocated by Bancroft, he would certainly have arrived at the ratio 74 : 26.

The author finds that the volume percentage of 74·04 holds when the aqueous phase is very weakly alkaline ($N/1000$—$N/500$). With more concentrated alkalis, higher ratios can be obtained, and Robertson's results can generally be repeated. The emulsions prepared with concentrated alkalis break up and a stable cream separates, which again has the volume ratio 74 : 26.

The phase ratios at the critical point with different strengths of alkalis were found to be:

TABLE IV.

Amount of alkali. C.c.	Amount of olive oil, 0·5 per cent. C.c.	Strength of alkali.	Volume ratio at inversion point.
25	*73·5*	*0·933N/1000*	*74 : 26*
20	58·4	0·933N/700	74·5 : 25·5
25	72·7	0·933N/500	74·4 : 25·6
20	75·2	0·933N/100	79 : 21
10	88·9	0·933N/50	89 : 11

It appears that the volume ratio is disturbed on account of the solid or gelatinous film which may be formed round the enclosed *particle when concentrated alkalis are used This solid can* further interfere by preventing the enclosed particles from coalescing and assuming any other size or shape. Further agitations, instead of making the globules more uniform, cause irregularities of shape.

Homogeneous Emulsions of Equal Particles.

Experiments were made in order to obtain homogeneous emulsions of particles of uniform size, and, after a long and careful study, it was found possible to obtain an emulsion in which most of the globules were equal spheres. It has been found that the best way to obtain an emulsion of this character is to select from a freshly prepared oil-in-water emulsion the cream which forms on standing undisturbed, and in which the volume ratios are close to 74 : 26. Very small quantities, from 5 c.c. to 10 c.c., were placed in a very carefully cleaned resistance-glass bottle and vigorously shaken for several hours by a powerful shaking machine. Samples were examined from time to time under the microscope until the particles were found to be very small and of nearly equal size. It was possible to preserve this character of the emulsion for several hours. It was found absolutely necessary to try these

operations only on freshly prepared emulsions, as emulsions which were allowed to remain for a day did not give such satisfactory results. This may be due to the ageing of the soap film, which makes it harder and more like a solid.

Three such homogeneous emulsions were prepared with different strengths of alkali, and measured quantities were decomposed by a drop of concentrated acid, and the volumes of the two phases measured in the measuring tube. The values of these, calculated from the radii of the globules on the assumption of closest packing and obtained practically, are tabulated in table V, and show a very fair agreement.

TABLE V.

Oil phase calculated from the equation for closest packing,

$$\frac{4\sqrt{2}\times r^3}{4\pi/3r^3} = \frac{\text{Total volume}}{\text{Oil phase}},$$ where r = radius of the globules.

Emulsion.	Total volume. C.c.	Strength of potassium hydroxide.	Radii of uniform particles. Mm.	Oil phase observed. C.c.	Oil phase calculated. C.c.
I.	7	$0·933N/500$	0·0075	5·09	5·1
II.	5	$0·933N/700$	0·0070	3·7	3·69
III.	5	$0·933N/1000$	0·0055	3·6	3·69

The results indicate that a weaker alkali yields a homogeneous emulsion of smaller globules. The size of the globule seems to depend on the concentration of the alkali if the shaking is constant. More work is necessary to establish this, and no conclusions can be drawn until sufficient data are available. It is intended to carry out further work on this important point by preparing larger quantities of homogeneous emulsions.

Effects of Electrolytes on Emulsions.

Clowes (*loc. cit.*) has demonstrated that suitably constituted emulsions of oil dispersed in water can be transformed into the reverse type of emulsions by shaking with a sufficient amount of calcium chloride or other calcium salts. He obtained some quantitative data, but his results are not sufficiently accurate on account of the method by which he studied inversion. A foreign substance like Sudan III had to be added, and the quantity of the emulsion was sensibly affected by the frequent removal of drops for examination under the microscope.

To ensure identical and comparable conditions, equal volumes of paraffin oil (B.P.) and water were used in all the following experiments. The paraffin oil contained 1 per cent. of oleic acid,

1 per cent. stearic and linoleic acids being also used. Emulsions were prepared in the mechanical shaker by shaking together equal volumes of oil and water in which varying proportions of potassium hydroxide and electrolytes were added previous to emulsification The volume of water and oil was always kept the same. A few results are tabulated below, the details and fuller discussion being reserved for a later contribution.

Table VI.

Effect of potassium hydroxide and barium nitrate on the emulsion equilibrium.

Volume of aqueous phase constant, 10 c.c.; volume of oil, 10 c.c. *Figures in the ammeter column; oil-in-water type.*

0—1 = inversion point.

0 = water-in-oil type. Voltage constant. Electrodes fixed.

Volume of $M/50$-KOH c.c.	Volume of $M/50$-$Ba(NO_3)_2$ in c.c.						
	0·2	0·4	0·6	0·8	1·0	1·2	1·4
1	0—1	0	0	0	0	0	0
2	10·2	0—1	0	0	0	0	0
3	11·2	10·8	0—1	0	0	0	0
4	12·1	11·2	10·7	0—1	0	0	0
5	13·0	12·7	11·8	10·9	0—1	0	0
6	14·1	13·0	12·8	17·1	10·7	0—1	0

Milliammeter reading.

Table VII.

Different Strength of the same Electrolyte.

Volume of $M/10$-KOH c.c.	Volume of $M/10$-$Ba(NO_3)_2$ in c.c.							
	0·1	0·25	0·3	0·4	0·6	0·8	1·0	1·5
1	12·1	0—1	0	0	0	0	0	0
2	13·0	12·7	11·9	11·0	0	0	0	0
3	13·9	13·0	12·3	11·9	11·0	0—1	0	0
4	14·6	13·7	13·0	12·1	11·7	—	—	—
5	15·5	14·7	13·9	13·0	12·1	11·9	11·7	0
6	16·3	15·3	14·8	14·0	13·0	12·0	11·7	0—1

Milliammeter reading.

Table VIII.

Linoleic Acid substituted in Place of Oleic Acid in Oil.

Volume of $M/10$-KOH c.c.	Volume of $M/10$-$Ba(NO_3)_2$ in c.c.							
	0·1	0·25	0·3	0·4	0·6	0·8	1·0	1·5
1	12·1	0—1	0	0	0	0	0	0
2	13·1	0—1	0	0	0	0	0	0
3	13·9	13·0	12·8	0—1	0	0	0	0
4	14·2	13·1	12·8	11·9	0	0	0	0
5	15·3	14·8	13·2	12·9	0—1	0	0	0
6	16·3	15·9	14·1	13·4	12·5	0—1	0	0

Milliammeter reading.

Other conditions as in tables VI and VII.

Clowes (*loc. cit.*) finds that emulsions of oil in water are produced whenever there are more than four molecules of sodium hydroxide to one of calcium chloride, emulsions of water-in-oil type whenever there are less than four molecules of the former to one of the latter, whilst at those points at which the ratio of sodium hydroxide to calcium chloride is exactly 4:1, neither type of emulsion predominates. The results indicated in tables VI or VII and VIII show that the ratio of potassium hydroxide to barium nitrate is exactly 4:1 in concentrations ranging from $M/10$-potassium hydroxide upwards. In lower concentrations the ratio is increased; for example, at $M/50$-potassium hydroxide it is about 5:1. Even the acid in oil appears to have some effect on the inversion point; for example, in table VIII, when linoleic acid is substituted for oleic acid, the ratio between potassium hydroxide and barium nitrate molecules is as 2:1. Employing this method, it will be easy to obtain much information on the effects of electrolytes on emulsion equilibrium in different concentrations and with different fatty acids.

These are effects the study of which is of great importance for a general theory of emulsification.

When de-emulsification takes place, the two phases separate and do not form an emulsion. De-emulsification is not easily and immediately detected by the eye, or by the methods of identification previously known. The electrical method is capable of indicating at once whether de-emulsification or coagulation has set in. If, on adding oil to an emulsion, it is found that the conductivity is increasing instead of decreasing, it is clear that the process of emulsification has stopped and the oil and the aqueous phase are separating, that is, de-emulsification has set in.

Further work on the effects of electrolytes on the emulsion equilibrium and the physical properties of emulsion is in progress.

Summary.

(1) A new method for the determination of inversion of phases and the identification of the two types of emulsion is described.

(2) Quantitative data on the effects of a few electrolytes on emulsion equilibrium have been obtained.

(3) The inversion point has been accurately determined with various oils and alkalis.

(4) It has been established that both types of emulsion are formed by sodium hydroxide and olive oil, and by sodium hydroxide and paraffin oil.

(5) Homogeneous emulsions have been obtained, and the equation for closest packing appears to hold in them.

(6) The effect of different fatty acids on the emulsion equilibrium is indicated in passing, details being reserved for a later contribution.

(7) It is shown that with weak alkali hydroxides the conditions governing the formation of type are dependent only on the phase ratio, and the special nature of the emulsifying agent exerts an effect only in high concentrations.

The author has pleasure in thanking Prof. F. G. Donnan for suggesting this research, and for his valuable guidance and kindly interest throughout the work. His thanks are also due to Mr. Higson for measuring the size of particles in homogeneous emulsions.

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LVIII.—*The Decomposition of Nitric Esters by Lime.*

By THOMAS MARTIN LOWRY, KENDALL COLIN BROWNING, and JOSHUA WILLIAM FARMERY.

Earlier Work on the Decomposition of Nitric Esters.

THE decomposition of nitric esters by water, acids, and alkalis has been investigated hy many workers.

(*a*) Van Kerckhoff and Reuter (*J. pr. Chem.*, 1847, **40**, 262) studied the decomposition of "pyroxylin" or nitrocellulose by steam at 100°, and obtained as a principal product a "typhoxylin" or "cellulose dinitrate" containing 6·66 per cent. of nitrogen; they also record the separation of a lead salt, which was almost certainly identical with the lead hydroxypyruvate prepared by a similar method and described in detail by Will forty-four years later (*Ber.*, 1891, **24**, 401); by heating pyroxylin with potassium hydroxide at 60°, potassium nitrate, potassium nitrite, and a sugar were formed.

(*b*) The production of potassium acetate and potassium formate, together with potassium nitrate and potassium nitrite in the ratio $KNO_3:2KNO_2$, was recorded by Hay (*Mon. Sci.*, 1873, [iii], **15**, 424), who accounted for the fact that five molecules of potassium

hydroxide were required for the decomposition of one molecule of nitroglycerin by putting forward the equation

$$C_3H_5O_9N_3 + 5KOH = KNO_3 + 2KNO_2 + CH_3{\cdot}CO_2K + H{\cdot}CO_2K + 3H_2O.$$

(*c*) Berthelot (*Compt. rend.*, 1900, **131**, 519) described the production of polymerisation-products of aldehyde by the action of solid potassium hydroxide on ethyl nitrate, and put forward (only to reject it in favour of an alternative view) the suggestion that the formation of nitrites in the action of potassium hydroxide on nitroglycerin might be due to a decomposition of the nitric ester into glyceraldehyde, as shown in the equation

$$C_3H_5(NO_3)_3 + 3KOH = C_3H_6O_3 + 2KNO_3 + KNO_2 + H_2O.$$

(*d*) Silberrad and Farmer (T., 1906, **89**, 1182, 1759) also detected acetic and formic acids, with nitric and nitrous acids, amongst the products of decomposition of 100 kilograms of nitrocellulose which had been stored at 54° during a period of twenty-three weeks; in addition, they proved the presence of ethyl nitrate, ethyl nitrite, and alcohol (perhaps derived from the alcohol–ether mixture used as a solvent in gelatinising the nitrocellulose), of butyric, dihydroxybutyric, oxalic, tartaric, and *iso*saccharic acids, and of a fermentable sugar, but they did not find either glycerol or cellulose amongst the products of decomposition of cordite by water or in presence of alkalis.

(*e*) Berl and Delpy (*Ber.*, 1910, **43**, 1421), by the action of alcoholic potassium hydroxide on nitroglycerin, obtained a glyceryl $\alpha\alpha'$-dinitrate, but were unable to detect either the mononitrate or glycerol itself.

(*f*) Klason and Carlson (*Ber.*, 1906, **39**, 2752), by the action of alcoholic sodium hydroxide on nitroglycerin in the presence of phenyl mercaptan, were able to recover glycerol, the mercaptan being oxidised to phenyl disulphide; by the same method they obtained from nitrocellulose a sample of cellulose of correct composition and free from nitrogen, whilst under similar conditions, ethyl nitrate gave the nitrate and nitrite of the alkali, but no trace of polymerised aldehyde. These observations are in line with the well-known fact that glycerol can be recovered from nitroglycerin by the action of sodium sulphide. A similar action to that of phenyl mercaptan is observed when hydrogen peroxide is added to the mixture (Carlson, *Ber.*, 1907, **40**, 4191); the hydrogen peroxide acts here as a reducing agent, just as it does towards potassium permanganate, and gaseous oxygen is liberated as a by-product.

Products of Decomposition of Cordite by Lime.

During the early months of 1919, the authors of this paper had an opportunity of examining the products obtained by the decomposition of cordite by means of lime in the presence of pyridine. The use of pyridine as a catalyst in this action was discovered by Prof. Hodgkinson, and no other substance is known which is equally effective in promoting the controlled decomposition of cordite. The product is a brown sludge, which can be dried in thin layers on a hot plate to a hard, brittle, porous mass resembling ginger-biscuits. Drying on a large scale is more difficult, but when the sludge is evaporated at a low temperature until it contains only about 17 per cent. of water, it solidifies on cooling, probably owing to the crystallisation of calcium nitrate in the form of the tetrahydrate, $Ca(NO_3)_2,4H_2O$, or the basic compound,

$$Ca(NO_3)_2,CaO,3H_2O$$

(Bassett and Taylor, T., 1914, **105**, 1926); after casting, the solid product will dry spontaneously in a warm atmosphere, and can then be powdered without difficulty.

In addition to ammonia and the oxides of nitrogen, which escape during the decomposition, the following products have been detected in the sludge:

(*a*) "*Cellulose Trinitrate.*"—When a half-decomposed cordite sludge is extracted with water and acid, and the dried residue is warmed with 95 per cent. alcohol and filtered, the addition of water to the alcoholic solution causes the precipitation of a yellowish-white, viscid precipitate, which contains $N = 9{\cdot}6$ per cent. and is highly inflammable. A similar substance has been described by Angeli (*Atti R. Accad. Lincei,* 1919, [v], **28**, i, 20), who obtained it by the addition of water to a solution of gun-cotton in pyridine (compare also Berl and Fodor, *Zeitsch. ges. Schiess.-u. Sprengstoffw.*, 1910, **5**, 254, 269). The formula $C_{12}H_{17}O_7(NO_3)_3$ requires $N = 9{\cdot}15$ per cent.

(*b*) "*Cellulose Dinitrate.*"—Analysis by the Schultze-Tiemann method of black charred rods remaining undecomposed after thirty-three hours' treatment with an insufficient supply of lime showed the presence of 6·7 per cent. of nitrogen as compared with 12·2 per cent. in the original nitrocellulose. The composition of this residue agrees in a remarkable way with the figure obtained by van Kerckhoff and Reuter (*loc. cit.*). The percentage of nitrogen required for the formula $C_{12}H_{18}O_8(NO_3)_2$ or $C_6H_9O_4{\cdot}NO_3$ is 6·76.

From these observations, it appears probable that the nitrocellulose, which contains originally four or five NO_3-groups for every twelve carbon atoms, is hydrolysed in successive stages to

mpounds containing three and two nitro-groups, but that after is point has been reached, the molecule decomposes completely.

(c) *Glycerol.*—Prof. Hodgkinson had already shown that lycerol could not be extracted as a by-product from the residues btained from the decomposition of cordite by lime and pyridine. Careful tests for the presence of glycerol were, however, carried out, in order to ascertain whether the toxicity to plants, which Dr. Russell reported in some of the earlier products, might not be due to the presence of glycerol in quantities insufficient for commercial recovery. A highly toxic solution obtained after forty-eight hours' treatment was found to contain no glycerol, and its toxicity was traced to the hydroxypyruvic acid which it contained (see below). A similar negative result was obtained on examining a sludge which had been heated during a period of only ten hours, at which stage practically all the nitroglycerin had disappeared, whilst most of the nitrocellulose was left unattacked in the form of brittle, porous rods.

In order to determine whether glycerol could be detected amongst the earliest products of decomposition, a special batch of sludge was prepared by heating, for one hour only at 95° to 100°, 450 grams of cordite clippings with the usual proportion of quicklime (225 grams), but using a very large excess of pyridine, namely, 4 litres of a 5 per cent. solution, that is, 44 per cent. of pyridine on the weight of cordite used instead of the usual proportion of 0·5 per cent. The decomposition was extremely rapid and complete; no traces of cordite could be seen at the end of one hour, and it was estimated that the action had proceeded at least as far as in twenty-four hours of treatment under ordinary conditions. The filtrate from this sludge was tested for glycerol, and traces of this compound were detected by the following tests:

(i) A drop of phenolphthalein was added to a 5 per cent. solution of borax; on adding the suspected liquid, the red colour was discharged, and, on boiling, it partly returned.

(ii) On heating the dry residue with potassium hydrogen sulphate, the choking odour of acrolein was noticed.

(iii) On heating with alkaline potassium permanganate, a partial reduction occurred.

(d) *Calcium Nitrate and Nitrite.*—A sample of sludge prepared by a similar method from 900 grams of cordite (with 22 per cent of its weight of pyridine), after one hour's heating, gave for the first time an excellent yield of colourless, crystalline calcium nitrate. It is therefore possible that the action of pyridine on cordite differs from that of alkalis and of lime in giving an appreci

able quantity of the products of direct hydrolysis, namely, glycerol and nitrates, and a much smaller proportion both of nitrites and of oxidised organic compounds; in other words, the decomposition by pyridine may perhaps be compared with that effected by alkali sulphides rather than by alkali hydroxides or by lime. The presence of nitrites is shown by the invariable liberation of oxides of nitrogen on acidifying the sludge.

(*e*) *Oxalic Acid.*—The fraction of the calcium salts which was soluble in hot dilute nitric acid, but insoluble in acetic acid, gave, after prolonged purification, a crystalline specimen of oxalic acid. A quantitative test by oxidation with potassium permanganate indicated that the calcium salts insoluble in acetic acid contained 62 per cent. of calcium oxalate.

(*f*) *Formic and Acetic Acids.*—Qualitative tests for these two acids gave in each case a positive result in only one of the tests applied, the other tests giving negative results. It is therefore clear that they can only have been present in very minute proportions, and that Hay's equations represent only a very minor part of the particular decomposition which we have studied.

(*g*) *Hydroxypyruvic Acid*, $HO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$.—After calcium oxalate and calcium nitrate and nitrite, the calcium salt of this acid appears to be the most important product of decomposition. Will prepared it by the decomposition of nitrocellulose, and it does not appear to have been described as a separate product of decomposition from nitroglycerin; on the other hand, the fact that it appears at a very early stage in the decomposition of cordite by lime and pyridine, and tends to disappear during the latter part of the decomposition, suggests that in this action it may be derived, at least in part, from nitroglycerin, to which it can be related by very simple equations.

Hydroxypyruvic acid was found to be present in every case in which the products of decomposition of cordite were reported as having a toxic action on plants, and a specimen of the calcium salt sent to Rothamsted for trial was reported as being extremely toxic. The presence of the acid was confirmed by preparing the osazone.

(*h*) *βγ-Dihydroxybutyric Acid.*—The residne from the preparation of the osazone, after removing the excess of phenylhydrazine by extraction with ether, can be re-precipitated as a lead salt and then converted into a calcium salt. This has the properties of the calcium salt of dihydroxybutyric acid (Silberrad and Farmer, *loc. cit.*), that is, the calcium salt is soluble, but gives an insoluble lead salt and does not yield an osazone; unlike the

lroxypyruvate, this calcium salt was proved not to be toxic to nts.

Che two calcium salts described under (*g*) and (*h*), instead of pearing as mere traces, like the formate and acetate, are often med in considerable quantities, and in one experiment alone a st-tube full of the mixed lead salts was separated.

Decomposition of Nitric Esters not a Simple Hydrolysis.

The object of bringing forward these observations and comaring them with earlier work on the same subject is to direct ttention to the wide divergence between the experimental facts nd the traditional theory in which the decomposition of nitric sters by alkalis is described as if it were a normal case of the ıydrolysis of an ester complicated only by secondary processes of ›xidation and reduction of the primary products.

The absence of glycerol as a product of decomposition of cordite is specifically referred to by Silberrad and Farmer, who made experiments under a variety of conditions, and also by Berl and Delpy in their study of the action of alcoholic potassium hydroxide on nitroglycerin. Prof. Hodgkinson also noticed at a very early period of his experiments that glycerol cannot be recovered as a product of the decomposition of cordite by lime in the presence of a small proportion of pyridine. Our own experiments fully confirm this conclusion, and a recent French patent, in which it was claimed that glycerol as well as sodium nitrate could be recovered from the products of the action of sodium hydroxide on mixtures of nitrocellulose and nitroglycerin "by the ordinary methods of the soap-manufacturer," was based on experiments with nitrocellulose powders only, and must be regarded as evidence rather of the optimism of the inventor than of the actual behaviour of nitroglycerin towards sodium hydroxide. The general experience seems to be that, in the absence of a reducing agent, glycerol is not regenerated.

This anomalous behaviour of nitroglycerin is repeated in nitrocellulose, which does not give any cellulose when decomposed by water or by alkalis (Silberrad and Farmer), as well as in simpler compounds, such as ethyl nitrate.

In order to account for this anomaly, whilst maintaining the view that the fundamental action is a hydrolysis or saponification of the normal type, a number of hypothetical reactions have been postulated. Thus, Silberrad and Farmer found it "somewhat surprising that no unchanged cellulose or glycerol should be

regenerated on hydrolysis, for if nitric acid is brought into contact with cellulose or glycerol in the concentrations which come into consideration in the hydrolysis, no oxidation occurs." They were therefore driven to the conclusion "that the nitric acid which has just been set free from the nitric ester is in a more active condition than nitric acid in its ordinary form."

In a similar way, Hay explained the production of potassium nitrate, nitrite, acetate, and formate by the action of potassium hydroxide on nitroglycerin as due to three consecutive actions, the second of which (a decomposition of glycerol by potassium hydroxide) is purely hypothetical, thus:

(i) A primary hydrolysis producing glycerol and potassium nitrate according to the equation

$$C_3H_5(NO_3)_3 + 3KOH = C_3H_8O_3 + 3KNO_3.$$

(ii) A hypothetical action, whereby the glycerol was converted by the action of the alkali hydroxide into potassium acetate and formate, together with water and "nascent hydrogen,"

$$C_3H_8O_3 + 2KOH = CH_3{\cdot}CO_2K + H{\cdot}CO_2K + H_2O + 4H,$$

using up two additional equivalents of potassium hydroxide (above those required for hydrolysis), as observed in his experiments.

(iii) A reduction by the nascent hydrogen of two-thirds of the potassium nitrate already produced,

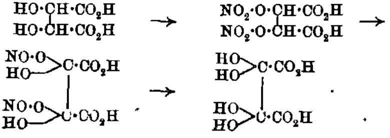
$$2KNO_3 + 4H = 2KNO_2 + 2H_2O.$$

Alternative Explanations of the Decomposition of Nitric Esters.

(*a*) As an alternative to the hypothetical "hydrolysis" represented by the equation

$$R{\cdot}CH_2{\cdot}O{\cdot}NO_2 + KOH = R{\cdot}CH_2{\cdot}OH + KNO_3,$$

Vignon and Maquenne (*Ann. Chim. Phys.*, 1891, [vi], **24**, 522) have assumed the intermediate formation and decomposition of an isomeric nitrite, $R{\cdot}CH(OH){\cdot}O{\cdot}NO$, which, by direct hydrolysis, would give rise to nitrous acid and a dihydroxy- (or carbonyl) compound, so that, for instance, the conversion of nitrotartaric acid into dihydroxytartaric acid may be represented by the following scheme:



This hypothesis has the disadvantage that no evidence has been produced of the concrete existence of the isomeric nitrite, and on many grounds we prefer the alternative views set out under (*b*) and (*c*) below. The paper is, however, important on account of the clear recognition by the authors of the fact that the decomposition of a nitric ester by an alkali may yield a ketone and a nitrite, instead of giving an alcohol and a nitrate as the primary products of decomposition.

(*b*) This alternative hypothesis was put forward in its simplest possible form in 1900 by Berthelot, who suggested that the decomposition of a nitric ester may proceed according to the equation

$$R\cdot CH_2\cdot O\cdot NO_2 + NaOH = R\cdot CHO + NaNO_2 + H_2O,$$

in place of the traditional equation

$$R\cdot CH_2\cdot O\cdot NO_2 + NaOH = R\cdot CH_2\cdot OH + NaNO_3.$$

Our own experiments, confirming as they do the observations of earlier workers, indicate that Berthelot's equation actually represents the main course of the decomposition; indications of a real hydrolysis are apparently confined to the production, as by-products, of partly hydrolysed compounds, such as Berl and Delpy's dinitrate and the lower cellulose nitrates described in the early part of the present paper.

(*c*) An elaboration of Berthelot's view was put forward a few years later by Klason and Carlson (*loc. cit.*), who suggested that the primary products are not the alcohol and a nitrate, thus:

$$C_2H_5\cdot O\cdot NO_2 + KOH = C_2H_5\cdot OH + KNO_3,$$

but an alcohol-peroxide and a nitrite,

$$C_2H_5\cdot O\cdot NO_2 + KOH = C_2H_5\cdot O\cdot OH + KNO_2.$$

In the ordinary course of events, the peroxide will decompose into an aldehyde and water,

$$CH_3\cdot CH_2\cdot O\cdot OH = CH_3\cdot CHO + H_2O;$$

but when a reducing agent, such as phenyl mercaptan, is present, the peroxide is reduced to the alcohol and the mercaptan is oxidised to phenyl disulphide,

$$CH_3\cdot CH_2\cdot O\cdot OH + 2C_6H_5\cdot SH = CH_3\cdot CH_2\cdot OH + H_2O + (C_6H_5)_2S_2.$$

In the same way, when hydrogen peroxide is present, the peroxide may be reduced to the alcohol, as shown in the equation

$$CH_3\cdot CH_2\cdot O\cdot OH + H_2O_2 = CH_3\cdot CH_2\cdot OH + H_2O + O_2.$$

(*d*) If it be assumed that the primary decomposition of a nitric ester yields either a peroxide or an aldehyde, together with a nitrite, instead of an alcohol and a nitrate, it is easy to account for many of the products which have actually been obtained by the decomposition. Thus, in the case of nitroglycerin, complete

decomposition on these lines would give rise to a compound containing three carbonyl groups:

$$C_3H_5(NO_3)_3 = CHO\cdot CO\cdot CHO + 3HNO_2.$$

From this intermediate compound, mesoxalic acid, reported by Berl *and* Delpy *as a product of "hydrolysis" of nitroglycerin by* alcoholic potassium hydroxide, could be produced by the normal oxidation of an aldehyde to an acid,

$$CO(CHO)_2 + O_2 = CO(CO_2H)_2;$$

the further oxidation of mesoxalic acid would yield oxalic acid, a principal product of decomposition in the case which we have studied. Hydroxypyruvic acid (the formation of which has, however, been recorded only in the case of nitrocellulose and of cordite and not from pure nitroglycerin) could be produced by a mere addition of the elements of water to the intermediate product formulated above:

$$CO(CHO)_2 + H_2O = HO\cdot CH_2\cdot CO\cdot CO_2H.$$

(*e*) In our experiments, the decomposition of nitroglycerin into acetic and formic acids takes place only to a very minute extent. The formation of traces of formic acid from the oxidised compounds set out above can be explained readily, but the production of acetic acid is a far more startling type of decomposition, since the formation of the methyl group in acetic acid necessarily involves a process of reduction in a medium in which the conditions appear to favour the oxidation rather than reduction of the organic constituents. It is conceivable that acetic acid and formic acid may be produced by the decomposition of pyruvic acid, formed by reduction from hydroxypyruvic acid,

$$CH_3\cdot CO\cdot CO_2H + 2KOH = CH_3\cdot CO_2K + H\cdot CO_2K + H_2O.$$

There is, however, more evidence for the decomposition of this acid into acetaldehyde and carbon dioxide,

$$CH_3\cdot CO\cdot CO_2H = CH_3\cdot COH + CO_2,$$

a change which has been postulated as an essential stage in alcoholic fermentation. In any case, the simultaneous oxidation and reduction which leads to the conversion of dextrose into carbon dioxide and alcohol finds strong analogies in the production, not only in the case of acetic acid, but also of butyric and dihydroxybutyric acids as products of the decomposition of nitrocellulose since both of these acids agree with acetic acid in containing a fully-reduced methyl or methylene group.

Summary.

Hydrolysis or saponification of the normal type is not the
ominant action when cordite is decomposed by lime in the
nce of pyridine.

) Traces of glycerol were detected only when a very large
ss of pyridine was used; these conditions were also the only
in which a clean, crystalline calcium nitrate was obtained.
calcium salt of hydroxypyruvic acid is, however, an important
luct of the action.

3) Two partly denitrated celluloses, corresponding approxim-
y with the formulæ $C_{12}H_{18}O_8(NO_3)_2$ and $C_{12}H_{17}O_7(NO_3)_3$, were
ained as by-products of incomplete decomposition, but no
ulose was obtained when the decomposition was carried to
npletion.

(4) It is therefore suggested that the main action is a decom-
sition of the nitric ester into a ketone or aldehyde and a nitrite,
stead of a hydrolysis to an alcohol and nitric acid.

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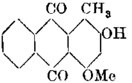
LIX.—*Note on the Constituents of* Morinda citrifolia.

By JOHN LIONEL SIMONSEN.

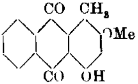
ALTHOUGH a number of investigations have been made of the constituents of *Morinda citrifolia* (compare T., 1918, **113**, 766), particularly by Oesterle, alone or in conjunction with Tisza (*Arch. Pharm.*, 1907, **245**, 287, 534; 1908, **246**, 150), no detailed examination of the root-bark of this species comparable with those conducted by Perkin and Hummel (T., 1894, **65**, 851) on *M. umbellata* and by Barrowcliff and Tutin on *M. longiflora* (T., 1907, **91**, 1909) has yet been made, and the author has thought it desirable to undertake this work.

It is necessary here to draw attention to a curious error in Barrowcliff and Tutin's communication. The hydroxymethoxymethylanthraquinone, melting at 290°, isolated by them, which yielded an acetyl derivative melting at 173°, is not, as they state, derived from 1:3-dihydroxy-2-methylanthraquinone, but is the monomethyl ether of rubiadin, since on hydrolysis it yielded a

dihydroxymethylanthraquinone, melting at 290°, which gave an acetyl derivative melting at 225° (compare Schunck and Marchlewski, T., 1894, **65**, 182). 1 : 3-Dihydroxy-2-methylanthraquinone also melts at 290°, but yields an acetyl derivative melting at 217—218°. It follows, therefore, that the hydroxymethoxymethylanthraquinone obtained by Barrowcliff and Tutin must be represented by either formula I or II, whilst the so-called 1 : 3-dimethoxy-2-methylanthraquinone is rubiadin dimethyl ether, 1 : 3-dimethoxy-4-methylanthraquinone.



(I.)



(II.)

The material available for investigation was the residue remaining after the extraction of morindin (T., 1918, **113**, 766).

Only two substances, namely, rubiadin monomethyl ether and alizarin *α*-methyl ether, could be isolated from the complex mixture which contained much resinous matter. The rubiadin monomethyl ether was identical with the substance isolated by Barrowcliff and Tutin from *M. longiflora*, and so far as the author is aware this substance has not been obtained from any other source. Alizarin *α*-methyl ether was first isolated by Perkin and Hummel (T., 1893, **63**, 1174) from *Oldenlandia umbellata*, and subsequently prepared synthetically by Oesch and Perkin (P., 1914, **30**, 213), whilst Barrowcliff and Tutin obtained it from *M. longiflora.*

The identity of the constituents of the root-bark of two plants so closely related as *M. citrifolia* and *M. longiflora* is of considerable interest. It is possible that the latter might at some period of its growth contain morindin, since the quantity of this glucoside appears to vary with the age of the bark. Thus the author has recently examined a specimen of *M. umbellata* which was quite free from colouring matter.

EXPERIMENTAL.

The material used for investigation was obtained by the acidification of the cold and hot water extracts of the sparingly soluble barium salt of morindin (compare Perkin and Hummel, *loc. cit.*, p. 858). The amorphous, yellow precipitates obtained in this way were examined separately, but as the constituents were found to be identical, except that the product precipitated from the hot water extract contained a large quantity of uncrystallisable resinous

ıatter, it is only necessary to describe in detail the investigation of he products isolated from the cold water extract.

The deep red aqueous solution of the barium salt was acidified with dilute hydrochloric acid, the solution boiled, and the flocculent, yellow precipitate allowed to settle, collected, and drained. After finely grinding and sifting, it was extracted with ether.* The ethereal extract was concentrated when, on keeping, a small quantity of a yellow solid (*A*) separated. This was collected, and the filtrate evaporated to dryness. The semi-solid residue was dissolved in the minimum quantity of hot methyl alcohol and allowed to remain for some days, when a yellow solid (*B*) was slowly deposited. This was collected, and the filtrate (*C*) reserved for further investigation (see below).

The yellow, semi-crystalline substances, *A* and *B*, which melted indefinitely at about 210°, were mixed and repeatedly crystallised first from alcohol and finally from acetic acid. In this manner golden-yellow needles were obtained which melted at 291° (0·1021 gave 0·2672 CO_2 and 0·0414 H_2O. C=71·4; H=4·5. $C_{16}H_{12}O_4$ requires C=71·6; H=4·5 per cent.).

This substance was clearly identical with the hydroxymethoxymethylanthraquinone (rubiadin monomethyl ether) described by Barrowcliff and Tutin (*loc. cit.*, p. 1912), who give the melting point as 290°. This was confirmed by the preparation of the acetyl derivative, which separated from ethyl acetate in long, yellow needles melting at 174° (Barrowcliff and Tutin give 173°). For analysis it was dried at 110° (0·11 gave 0·282 CO_2 and 0·0444 H_2O. C=69·9; H=4·5. $C_{18}H_{14}O_5$ requires C=69·7; H=4·5 per cent.).

For the conversion of the rubiadin monomethyl ether into rubiadin the following method was found to yield the most satisfactory results. The ether (0·5 gram) was mixed with concentrated hydrochloric acid (5 c.c.) and heated for two hours in a sealed tube at 140—150°. The crude product was collected, and boiled with an aqueous solution of barium hydroxide, when the sparingly soluble barium salt of rubiadin separated. This was decomposed with dilute hydrochloric acid, and the rubiadin purified by crystallisation from alcohol, when it was obtained in needles melting at 290° and yielding an acetyl derivative which separated from ethyl acetate in fine, yellow needles melting, as stated by Schunck and Marchlewski (*loc. cit.*, p. 184), at 225°.

The methyl-alcoholic filtrate (*C*), from which the rubiadin methy ether had been separated, was evaporated to dryness, and the red resinous residue acetylated by boiling with acetic anhydride contair

* The residue consisted of resinous matter from which nothing crystallir could be isolated.

ing a drop of pyridine. After removing the acetic anhydride, the crude acetyl derivative was triturated with much ether, when a quantity of a yellow solid remained undissolved. This was separated, the ethereal solution, after washing with sodium carbonate solution which removed a little resinous matter, concentrated and allowed to remain, when a further quantity of a yellow solid was deposited. This was collected and mixed with the yellow solid mentioned above. The filtrate on further concentration yielded only resinous substances, from which nothing crystalline could be isolated.

The yellow acetyl derivative was purified by repeated crystallisation, first from alcohol, and finally from ethyl acetate, when it was obtained in silky, yellow needles melting at 209—210°, and evidently consisted of the acetyl derivative of alizarin monomethyl ether (Perkin and Hummel, T., 1893, **63**, 1174; Barrowcliff and Tutin, *loc. cit.*, p. 1914) (Found, C=69·1; H=4·1. $C_{17}H_{12}O_5$ requires C=68·9; H=4·0 per cent.).

On hydrolysis the acetyl derivative yielded alizarin α-methyl ether, which melted at 177—178°, and the latter when boiled with an aqueous solution of barium hydroxide gave alizarin, which was recognised by the usual tests.

The author wishes to thank Mr. M. Gopal Rau for his assistance.

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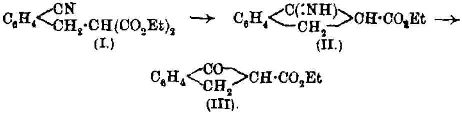
LX.—*Syntheses with the Aid of Monochloromethyl Ether. Part IV. The Condensation of Ethyl Benzyl Sodiomalonate and Monochloromethyl Ether.*

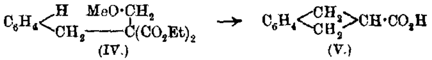
By JOHN LIONEL SIMONSEN.

THE conversion of substituted ethyl benzylacetates into derivatives of hydrindene takes place with comparative ease. Thus, Mitchell and Thorpe (T., 1910, **97**, 2263) have shown that ethyl *o*-cyanobenzylmalonate (I), when warmed with a trace of sodium ethoxide in alcoholic solution, is converted quantitatively into ethyl 1-imino-

hydrindene-2-carboxylate (II), which, on treatment with hydrochloric acid, yields ethyl 1-hydrindone-2-carboxylate (III).



It appeared to the author to be a matter of some interest to investigate the properties of *ethyl benzylmethoxymethylmalonate* (IV), since it seemed possible that this ester might on hydrolysis lose methyl alcohol, with the formation of hydrindene-2-carboxylic acid (V).



The required ester was readily obtained in an excellent yield by the condensation of ethyl benzylsodiomalonate and monochloromethyl ether. On hydrolysis with alcoholic potassium hydroxide, it gave *benzylmethoxymethylmalonic acid*, which decomposed at 160—162°, with the formation of *β-phenyl-α-methoxymethylpropionic acid*. All attempts to convert the methoxy-acid into the hydrindenecarboxylic acid were unsuccessful. When heated with concentrated hydrochloric acid, *α-benzylacrylic acid* was obtained, and the same acid was formed when ethyl benzylmethoxymethylmalonate or benzylmethoxymethylmalonic acid were heated with mineral acids.

It is clear from the above that ethyl benzylmethoxymethylmalonate shows properties similar to those of the methoxymethyl esters described in Part *III* of this series (T., *1915*, **107**, *783*), and shows no tendency to undergo ring-formation on hydrolysis. It had been intended to extend these experiments to derivatives of ethyl benzylmalonate with negative groups in the aromatic nucleus, but as there is little prospect of the author being able to continue the work in the near future, it has appeared desirable to publish the results obtained in their present, somewhat incomplete, form.

Experimental.

Ethyl Benzylmethoxymethylmalonate (IV).

Ethyl benzylmalonate (25 grams) was gradually added to finely divided sodium (2·3 grams) suspended in dry ether (200 c.c.), when the sodium rapidly dissolved and a clear solution of the sodium

compound of ethyl benzylmalonate was obtained. Monochloromethyl ether (8 grams) dissolved in twice its volume of dry ether was cautiously added, when a vigorous reaction took place, which was controlled by cooling in ice-water. Next day water was added to dissolve the colloidal sodium chloride, the ether separated, dried, and evaporated. The residual oil was distilled under diminished pressure, when practically the whole passed over at 194—200°/18 mm. On redistillation, the oil boiled constantly at 194—195°/19 mm. (yield, 23 grams):

0·0988 gave 0·2358 CO_2 and 0·0676 H_2O. C=65·1; H=7·6.
$C_{16}H_{22}O_5$ requires C=65·3; H=7·5 per cent.

This ester was obtained as a very viscid oil, which, on keeping for some weeks, crystallised in massive plates melting at about 49—50°. Owing to its ready solubility in all the ordinary organic solvents, it was not found possible to recrystallise it.

Hydrolysis of Ethyl Benzylmethoxymethylmalonate. I. *With Potassium Hydroxide. Benzylmethoxymethylmalonic Acid.*

In performing this hydrolysis, the ester (5 grams) was mixed with methyl-alcoholic potassium hydroxide solution (2·5 grams of KOH) and allowed to remain in the cold overnight, when a sparingly soluble *potassium* salt (*A*) separated in fine needles. This was washed with a little methyl alcohol, and the filtrate heated on the water-bath for one hour, when a further quantity of the potassium salt separated, which was added to *A*.*

The potassium salt was dissolved in water and the solution faintly acidified with hydrochloric acid, when an acid separated as a viscid oil, which rapidly crystallised, and was recrystallised from a mixture of ether and light petroleum:

0·0886 gave 0·1952 CO_2 and 0·0495 H_2O. C=60·1; H=6·2.
$C_{12}H_{14}O_5$ requires C=60·5; H=5·9 per cent.

Benzylmethoxymethylmalonic acid crystallised in stellate needles decomposing at 160—162°. It was readily soluble in ether, chloroform, or benzene, but only sparingly so in water or light petroleum. It yielded a sparingly soluble, amorphous *barium* salt; the *calcium* salt was obtained as a sparingly soluble, caseous, white precipitate, which appeared to be microcrystalline:

* The filtrate from the potassium salt was saturated with carbon dioxide, the alcohol removed on the water-bath, and the aqueous solution acidified, when an oil separated which partly solidified. The solid was collected and found to consist of benzylmethoxymethylmalonic acid. The oily acid was obtained in too small a quantity for investigation.

0·7088 lost 0·2121 H_2O at 120°. H_2O = 29·9.

0·3123 gave 0·1068 $CaSO_4$. Ca = 10·0.

$C_{12}H_{12}O_5,6\frac{1}{2}H_2O$ requires H_2O = 29·9; Ca = 10·2 per cent.

0·1029 Gram neutralised 0·0735 gram of barium hydroxide, hereas a dibasic acid, $C_{12}H_{14}O_5$, should neutralise 0·074 gram.

As has been mentioned above, benzylmethoxymethylmalonic cid melted with decomposition, this being due to loss of carbon lioxide with the formation of the monobasic acid, *β-phenyl-α-nethoxymethylpropionic acid*. This acid has, so far, only been obtained as a viscid oil. In one experiment, the dibasic acid 0·775 gram) was heated at 165° until all evolution of carbon lioxide had ceased, when a loss in weight of 0·142 gram was observed, whereas this weight of a dibasic acid should lose 0·139 gram in passing to a monobasic acid. A further proof of the formation of the monobasic acid was furnished by the analysis of the *silver* salt, which separated from a faintly alkaline solution as a granular, white powder:

0·1991 gave 0·0727 Ag. Ag = 36·5.

$C_{11}H_{13}O_3Ag$ requires Ag = 35·9 per cent.

When benzylmethoxymethylmalonic acid was boiled for some hours with hydrochloric acid (50 per cent.), it was converted into *α-benzylacrylic acid* (see below), and this was found to be the simplest method for the preparation of this acid.

II. *With Hydrochloric Acid. α-Benzylacrylic Acid*, $CH_2Ph\cdot C(:CH_2)\cdot CO_2H$.

Ethyl benzylmethoxymethylmalonate was hydrolysed by hydrochloric acid only with great difficulty. The ester (20 grams) was mixed with hydrochloric acid (100 grams), acetic acid (25 grams), and water (50 c.c.), and the mixture heated under reflux for thirty-six hours. The oil was dissolved in ether, and the acid removed from the ethereal solution by washing with sodium carbonate solution, from which, on acidification, 2·5 grams of an oily acid* were obtained. The ether was evaporated, and the residual oil mixed with methyl-alcoholic potassium hydroxide solution (7 grams of KOH), when, on keeping, the sparingly soluble potassium salt of benzylmethoxymethylmalonic acid separated. The filtrate from this salt was saturated with carbon dioxide, the alcohol removed by evaporation, and the aqueous solution rendered just acid with hydrochloric acid, when an oil separated which rapidly solidified.

* The oily acid partly solidified and, after draining on porous porcelain, the crystals were found to consist of α-benzylacrylic acid.

The solid was purified by repeated crystallisation from dilute methyl alcohol:

0·1586 gave 0·43 CO_2 and 0·0876 H_2O. C=73·8; H=6·1.

$C_{10}H_{10}O_2$ requires C=74·1; H=6·1 per cent.

α-Benzylacrylic acid separated in glistening prisms, which melted at 68—69°. It was readily soluble in all the ordinary organic solvents, but only very sparingly so in water.

On titration, 0·1109 gram neutralised 0·0589 gram of barium hydroxide, whereas a monobasic acid, $C_{10}H_{10}O_2$, should neutralise 0·0587 gram.

That this acid was not identical with the isomeric α-methylcinnamic acid melting at 74° was shown by the fact that a mixture of the two melted at 40°. Further, these two acids are readily distinguished in that α-benzylacrylic acid yields a readily soluble barium salt, whereas the barium salt of α-methylcinnamic acid is only sparingly soluble.

In alkaline solution, α-benzylacrylic acid is unstable towards potassium permanganate; when dissolved in chloroform, it readily absorbs bromine, with considerable evolution of heat. In one experiment, the acid (0·5 gram) was dissolved in chloroform (3 c.c.) and treated with the calculated quantity of bromine in chloroform solution. On keeping, the *bromo*-acid separated, and was purified by crystallisation either from chloroform or dilute acetic acid:

0·1196 gave 0·14 AgBr. Br=49·8.

$C_{10}H_{10}O_2Br_2$ requires Br=49·7 per cent.

*αβ′-Dibromo-β-phenyl*iso*butyric acid*, $CH_2Ph\cdot CBr(CH_2Br)\cdot CO_2H$, crystallised in fine needles melting at 145—146°. When reduced with sodium amalgam, it yielded β-phenyl*iso*butyric acid, which was identified by conversion into the characteristic amide melting at 107°, and this melting point was not altered by admixture with a specimen of the amide from another source (Found: N=8·6. Calc.: N=8·5 per cent.).

*β′-Bromo-β-phenyl*iso*butyric Acid.*—This acid was formed when α-benzylacrylic acid was mixed with an acetic acid solution of hydrogen bromide (saturated at 0°) and heated in a sealed tube at 100° for two hours. On pouring into water, a heavy oil separated, which was dissolved in ether, the ethereal solution washed to remove acetic acid, dried, and evaporated, when a viscid oil was obtained. After remaining for some days in a vacuum desiccator, it was analysed, and was evidently nearly pure:

0·1455 gave 0·1037 AgBr. Br=30·3.

$C_{10}H_{11}O_2Br$ requires Br=32·9 per cent.

The bromo-acid dissolved readily in potassium hydroxide solution · ammonia, but, on warming, the solution clouded, owing probbly to the separation of the hydrocarbon; the acid was, however, uuch more stable than its isomeride (see below).

When dissolved in concentrated aqueous ammonia and allowed o remain for some days in the cold, it was converted quantitatively nto *β′-amino-β-phenyl*iso*butyric acid.* For analysis, it was reystallised from chloroform:

0·1587 gave 11·6 c.c. N_2 at 32° and 760 mm. N=7·8.

$C_{10}H_{13}O_2N$ requires N=7·8 per cent.

This acid separated from chloroform in glistening leaflets melt-ng at 128°. It was readily soluble in water or alcohol, more sparingly so in the ordinary organic solvents.

*β-Bromo-β-phenyl*iso*butyric Acid*, CHBrPh·CHMe·CO_2H.—For purposes of comparison, this bromo-acid, which does not appear to have been described previously, was prepared from α-methylcinnamic acid by the action of an acetic acid solution of hydrogen bromide in the manner described above. On pouring the mixture into water, a solid separated, which crystallised from formic acid in glistening prisms melting at 168—170°:

0·1347 gave 0·1037 AgBr. Br=32·7.

$C_{10}H_{11}O_2Br$ requires Br=32·9 per cent.

Like other β-bromo-acids, this acid reacted very readily with alkalis. When dissolved in cold sodium carbonate solution, the solution rapidly clouded, with the separation of an oil, and the same behaviour was observed with ammonia, so that it was not found possible to prepare the amino-acid.

In one experiment, the oil formed by the action of dilute sodium carbonate solution was separated, dissolved in chloroform, and treated with a chloroform solution of bromine, when, on allowing the solvent to evaporate, needles were obtained which melted at 65—66°, and evidently consisted of the dibromide derived from allylbenzene, which had resulted from the action of the alkali on the bromo-acid (Found: Br=57·9. Calc.: Br=57·5 per cent.).

The author wishes to thank Mr. M. Gopal Rau for assistance in the analytical work.

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DEHRA DUN, INDIA. [*Received, April 8th, 1920.*]

LXI.—*The Constituents of Indian Turpentine from* Pinus longifolia, *Roxb. Part I.*

By John Lionel Simonsen.

The manufacture of turpentine in India from the oleo-resin of *Pinus longifolia*, Roxb., is now an established industry, and large quantities of the oil are distilled in the Government factories at Jallo in the Punjab and Bareilly in the United Provinces. The oil, whilst quite suitable for the majority of technical purposes, is regarded as inferior to American turpentine, owing to the residue which it leaves on evaporation and to its proneness to oxidation.

The constituents of Indian turpentine have already formed the subject of several investigations (Rabak, *Pharm. Rev.*, 1905, **23**, 229; Schimmel's *Bericht*, April, 1906, 66; October, 1911, 93; *Bull. Imp. Inst.*, 1911, **9**, 8; Robinson, P., 1911, **27**, 247; Singh, *Ind. For. Rec.*, 1912, **4**, Pt. I), which have established the presence of *l*-α-pinene, β-pinene, a terpene yielding sylvestrene hydrochloride when treated with hydrogen chloride, and a sesquiterpene. Although in the literature it is definitely stated that sylvestrene is present (compare Parry, "Essential Oils," Vol. I, p. 18), yet Robinson (*loc. cit.*), to whom we owe the most careful investigation of the oil that has been made up to the present, drew the conclusion that the fraction previously assumed to contain sylvestrene in all probability contained some isomeric terpene, which on treatment with hydrogen chloride yielded sylvestrene hydrochloride. He also suggested that dipentene was probably present.

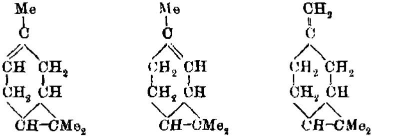
In view of the above results, it appeared to the author desirable that a careful re-examination of the constituents of Indian turpentine should be made, and the results so far obtained form the subject of this communication.

The oil used was distilled at the Government turpentine factory at Jallo, and was specially collected under the supervision of Mr. A. J. Gibson, Indian Forest Service, the officer in charge of the factory. It was carefully sealed up immediately after distillation in five-gallon drums, and prior to use it was dried for some days over anhydrous magnesium sulphate.

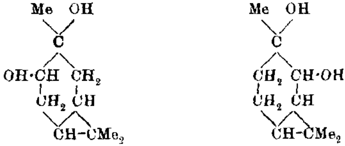
On careful fractional distillation, the presence of the following constituents was definitely proved: *l*-α-pinene, β-pinene, a new bicyclic terpene, for which the name *d-carene* is proposed, and a tricyclic sesquiterpene, *longifolene*.

The hydrocarbon, *d*-carene, which is without doubt identical with the hydrocarbon described by Robinson (*loc. cit.*), is an oil

›iling at 168—169°/705 mm., and possessing a characteristic and ›rious, sweet odour. The constitution of this new terpene was ›termined by investigating its behaviour on treatment with ydrogen chloride and on oxidation with potassium permanganate. Vhen treated in ethereal solution with hydrogen chloride, an oily ydrochloride was obtained, which partly solidified on cooling in a reezing mixture. The solid was found to be pure *d*-sylvestrene ydrochloride melting at 72°, whilst the terpene obtained from the iquid hydrochloride on removal of the hydrogen chloride in the ısual manner (see p. 575) was found to be a mixture of sylvestrene ınd dipentene. The latter was identified by means of the tetrabromide after removing the greater part of the sylvestrene by treatment with potassium dichromate and sulphuric acid in the manner suggested by Baeyer (*Ber.*, 1894, **27**, 810, 3485). The formation of a mixture of sylvestrene and dipentene hydrochlorides is most simply explained if it is assumed that the new terpene is represented by one of the three following formulæ (I, II, or III),



(I.) (Δ³-Carene.) (II.) (Δ⁴-Carene.) (III.) (Dehydrocarane.)

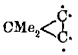


(IV.) (V.)

since it is obvious that a bicyclic terpene possessing one of these structures would, on fission of the *cyclo*propane ring, yield a mixture of the hydrochlorides of the monocyclic terpenes.

Further evidence in support of the above view was furnished by a study of the products formed on oxidation with potassium permanganate. When oxidised in the presence of alkali in ice-cold solution, the main product of the oxidation was found to be a *glycol*, $C_{10}H_{18}O_2$, melting at 69—70°. This glycol does not

appear to contain a primary alcohol group, since, in benzene solution, it does not react with phthalic anhydride, and it follows, therefore, that *d*-carene cannot be represented by formula III, and that the glycol must have either formula IV or V. All attempts to convert the glycol into a ketone by oxidation with chromic acid were unsuccessful, the reaction proceeding apparently abnormally with the formation of oils of high boiling point, from which nothing crystalline could be isolated. The alkaline liquid from which the glycol had been separated was acidified, and the acids formed during the oxidation carefully examined. The main product was a viscous oil, but two crystalline acids were obtained. Owing to the small yield, one of these, melting at 137°, could not be identified, but the second acid was found to be dimethylmalonic acid, thus proving definitely the presence of the grouping



in *d*-carene.

In the light of these observations, it appeared desirable to attempt to isolate caronic acid, and *d*-carene was therefore oxidised with potassium permanganate in the manner adopted by Baeyer and Ipatiev (*Ber.*, 1896, **29**, 2796) for the preparation of this acid from carone. The product of the oxidation was a viscous oil, from which nothing crystalline separated, and evidently did not contain any *cis*-caronic acid, but, on conversion into the ammonium salt, a small quantity of a crystalline salt was obtained, which was only sparingly soluble in cold water, and crystallised in glistening prisms. On acidification, an acid crystallising in prisms and melting at 212—213° was obtained, and there can be no doubt that this was *trans*-caronic acid, which is stated by Baeyer and Ipatiev to melt at this temperature (see p. 577).

So far as the author is aware, *d*-carene is the first naturally occurring terpene which has been found to contain the carane ring, and is therefore of more than usual interest. It has not been found possible to decide whether formula I or II correctly represents the structure of this terpene, and it does not appear unlikely that, as is assumed to be the case with sylvestrene, the hydrocarbon may be a mixture of the two isomerides. The molecular refraction was found to be 44·22, which agrees well with that calculated (44·19) for a compound containing a *cyclo*hexane and a *cyclo*propane ring. The fact that the molecular refraction is practically normal points to the absence of conjugation of a double bond with the *cyclo*propane ring and renders it probable that *d*-carene is represented by formula I (d-Δ^3-carene). It is hoped to prepare

synthetically the hydrocarbon represented by formula II (Δ^4-carene), and experiments in this direction are in progress.

The sesquiterpene for which the name *longifolene* is proposed has up to the present only been cursorily examined. It yields very beautiful derivatives with hydrogen chloride, hydrogen bromide, and hydrogen iodide, and from a consideration of its molecular refraction (M = 64·15) it is evidently tricyclic.

EXPERIMENTAL.

The oil used for these experiments was reddish-brown, and, after drying over magnesium sulphate, had the following constants: D_{30}^{30} 0·8717, n_D^{30} 1·4725, α_D −2·38°, acid value 2·4.

A large quantity was submitted to a careful fractional distillation under diminished pressure, using a twelve-pear Young still-head, when it was readily separated into the following three fractions: up to 118°/200 mm. (31 per cent.), 118—130°/200 mm. (47·6 per cent.), 149—155°/36 mm. (10·2 per cent.); loss and residue (by difference), 11·2 per cent.

The fractions boiling below 130°/200 mm. were carefully refractionated under the ordinary pressure, and were divided into two main fractions, *A* distilling at 155—167°/706 mm. (60·8 per cent.) and *B* at 167—171°/706 mm. (14·8 per cent.). Fraction *A* consisted mainly of α- and β-pinene, and a pure fraction of *l*-α-pinene was isolated boiling at 153—154°/700 mm. and possessing the following constants: D_{27}^{27} 0·8525, n_D^{28} 1·4625, α_D −34°, which agree well with those usually found for this hydrocarbon. The identity was further confirmed by the formation of α-pinonic acid on treatment with potassium permanganate in the usual manner. The presence in fraction *A* of β-pinene was proved by the isolation of nopinic acid (m. p. 128°) from the products of the oxidation with potassium permanganate in the usual manner.

d-*Carene* (d-Δ^3- or -Δ^4-*Carene*).

The fraction *B* (see above) was found on repeated fractionation to yield an oil, which boiled quite constantly at 168—169°/705 mm., 123—124°/200 mm. This hydrocarbon, for which the name *d*-carene is proposed, was found to have the following constants: D_{30}^{30} 0·8586, n_{30} 1·469, α_D +7·69°. M = 44·23, calc. for $C_{10}H_{16}|^{-}$ = 43·5, which, with the increment for the presence of a *cyclo*propane ring (0·69), becomes 44·19 (compare Eisenlohr, "Spektrochemie der organischen Verbindungen," p. 131).

Another sample of *d*-carene from a different sample of turpen-

tine was found to have the following constants: D_{27}^{27} 0·8594, n_D^{27} 1·47, α_D +7·83°.

Owing to the readiness with which *d*-carene is oxidised on exposure to the air, only approximate figures were obtained on analysis. A specimen distilled three times over sodium under diminished pressure and analysed immediately gave the following figures:

0·1019 gave 0·327 CO_2 and 0·107 H_2O. C=87·5; H=11·7.
$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

d-Carene is a colourless oil possessing a very characteristic, somewhat sweet odour. When dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, a transient, green coloration was observed. Unlike sylvestrene and terpinene, it was found not to be acted on by a mixture of potassium dichromate and sulphuric acid. The ease with which it undergoes oxidation was shown by the fact that when 1 c.c. was placed in a closed vessel, it absorbed all the oxygen present in three days.

In chloroform solution, *d*-carene readily absorbed bromine, but after the addition of one molecular proportion, the absorption became very slow and hydrogen bromide commenced to be evolved. It was not found possible to obtain a solid bromo-derivative, whilst the nitrosochloride and the nitrosite could also only be obtained as oils; it yielded, however, a crystalline *nitrosate*. The terpene (5 grams) was mixed with acetic acid (2 c.c.) and amyl nitrite (4 grams), and nitric acid (D 1·4) (3·5 grams) was then added very slowly to the well-cooled mixture. A solid was slowly deposited, and, after an hour, alcohol was added and the solid collected. It was purified by crystallisation from a mixture of chloroform and light petroleum, when it was obtained in glistening prisms which decomposed at 141·5°:

*0·089 gave 11 c.c. N_2 at 34° and 741 mm. N=12·8.
$C_{10}H_{16}O_3N_2$ requires N=13·2 per cent.

d-*Carene nitrosate* is very sparingly soluble in methyl and ethyl alcohols or light petroleum, more readily so in acetone or chloroform.

d-Carene showed no tendency to undergo hydration when treated with dilute sulphuric acid. In one experiment, the terpene (20 grams) was heated at 100° for seven days with dilute sulphuric acid (5 per cent.) (100 c.c.) in a closed vessel from which the air had been displaced by carbon dioxide. The terpene distilled completely at 123—124°/200 mm., and that it was quite unaffected

* I wish to thank Prof. B. K. Singh for this analysis.

by the treatment is indicated by the following constants: D_{30}^{30} 0·8595, n_D^{30} 1·469.

Action of Hydrogen Chloride on d-*Carene*.

As has already been mentioned, *d*-carene on treatment with hydrogen chloride gives a mixture of *d*-sylvestrene and dipentene hydrochlorides. In one experiment, the terpene (30 grams) was dissolved in dry ether (60 c.c.), and dry hydrogen chloride passed into the well-cooled solution until it was saturated. After two days, the ether was removed in a vacuum, and the residual brown oil cooled in a freezing mixture, when it partly solidified. The crystals were rapidly collected, and, after draining on porous porcelain, were found to melt at 71° (yield, 6 grams). On recrystallisation from methyl alcohol, the hydrochloride separated in glistening needles melting at 72°, and evidently consisted of sylvestrene hydrochloride. In chloroform solution, $[\alpha]_D$ had the value +20·31° (Found: Cl=33·7. $C_{10}H_{18}Cl_2$ requires Cl=33·9 per cent.). A quantity of the hydrochloride was converted into the terpene, which was found to possess all the properties ascribed to *d*-sylvestrene.

The liquid hydrochloride (40 grams) from which the *d*-sylvestrene hydrochloride had been separated was mixed with acetic acid (80 grams) and sodium acetate (40 grams) and heated for thirty minutes on the sand-bath. The hydrocarbon was distilled in a current of steam, separated, and, after boiling for a short time with potassium hydroxide solution, extracted with ether, the ether dried and evaporated, and the residual oil distilled at 200 mm., when 12 grams of an oil were obtained distilling between 120° and 140°. The hydrocarbon, which had a pleasant odour of lemons, gave, when dissolved in acetic acid, an intense sylvestrene coloration with sulphuric acid. In order to remove the greater portion of the sylvestrene, the mixture of terpenes was repeatedly shaken (twenty times) with small quantities of dilute potassium dichromate solution (compare Baeyer, *loc. cit.*). After drying over potassium carbonate, the remaining oil was distilled over sodium, when the greater portion passed over at about 130°/200 mm. (yield, 5 grams). The terpene, which still gave the sylvestrene reaction, although much less markedly than before, was dissolved in chloroform and treated with a chloroform solution of bromine until a permanent straw coloration was obtained, the chloroform removed in a vacuum, and the residual viscid oil cooled in a freezing mixture, when it rapidly crystallised. After draining on porous porcelain, the bromo-derivative was purified by crystallisation from ethyl acetate, when it was found to melt at

123—124°, and this melting point was not depressed on admixture with a specimen of dipentene tetrabromide from another source (Found: Br = 70·6. $C_{10}H_{16}Br_4$ requires Br = 70·2 per cent.).

Oxidation of d-*Carene*: 1. d-*Carene Glycol* (IV *or* V).

The terpene (50 grams) was mixed with sodium hydroxide solution (500 c.c.; 50 grams of NaOH), and, after the addition of ice, potassium permanganate solution (1·5 litres; 116 grams of $KMnO_4$) was gradually added with constant shaking, the solution being kept at 0° during the addition. The oxidation, which proceeded rapidly at first, became very slow towards the end. When the colour of the potassium permanganate had disappeared, steam was passed into the solution to remove the unchanged terpene (20 grams), the solution filtered, and concentrated on the water-bath, carbon dioxide being passed into the liquid during evaporation. The alkaline solution was extracted ten times with ether to remove the neutral products formed during the oxidation, the ethereal extract dried over potassium carbonate, the ether evaporated, and the residual oil distilled under diminished pressure, when practically the whole passed over at 166—167°/42 mm. On keeping, the viscous oil rapidly crystallised in long needles melting at 69—70°:

0·1402 gave 0·361 CO_2 and 0·131 H_2O. C = 70·2; H = 10·4.
$C_{10}H_{18}O_2$ requires C = 70·6; H = 10·6 per cent.

d-*Carene glycol* is readily soluble in all the ordinary organic solvents, and it was not found possible to recrystallise it. In chloroform solution it has $[\alpha]_D$ +16·05. *d*-Carene glycol does not react with phthalic anhydride when heated in benzene solution on the water-bath, and it is therefore extremely unlikely that it contains a primary alcohol group. When mixed with sulphuric acid (D 1·25) it readily dissolved, and on keeping a viscid oil separated which could not, however, be obtained crystalline. It reacted readily with hydrogen bromide, but the product could not be obtained solid. In acetic acid solution it was oxidised by chromic acid with the formation apparently of a complex mixture, from which, owing to the small quantity of material at the author's disposal, nothing definite could be isolated.

The alkaline liquid from which the glycol had been separated was acidified with dilute sulphuric acid and repeatedly extracted with ether. On removal of the ether a viscid oil remained which had a strong odour of butyric acid. As the oil showed no tendency to crystallise it was esterified in the usual manner with alcohol and sulphuric acid, and the resulting mixture of esters carefully frac-

tionated under diminished pressure (44 *mm.*). A small quantity distilled below 160°, and three main fractions were collected: *A* at 160—170°, *B* at 170—185°, and *C* at 180—200°.

Fraction A, which was a pleasant-smelling oil, was hydrolysed with alcoholic potassium hydroxide solution in the usual manner, and after removal of the alcohol and acidification the aqueous solution was repeatedly extracted with washed ether, the ethereal extract dried and evaporated, when an oil was obtained which rapidly solidified. After draining on porous porcelain, the acid was recrystallised from water, when it separated in small plates which decomposed at 186—187° and evidently consisted of dimethylmalonic acid (Found, C = 45·2; H = 5·8. $C_5H_8O_4$ requires C = 45·4; H = 6·1 per cent.).

The view that this acid was dimethylmalonic acid was confirmed by the fact that when mixed with a specimen of dimethylmalonic acid from another source no depression of the decomposition point was observed.

Fraction *B*, which was a somewhat viscous, unpleasant-smelling oil, was hydrolysed with alcoholic potassium hydroxide solution, and the acid obtained in this way was isolated by extraction with ether in the usual manner. The acid was a very viscous, unpleasant-smelling oil, which on trituration with a little water partly solidified. The solid was separated, drained on porous porcelain, and purified by crystallisation from dilute methyl alcohol, when it crystallised in long, prismatic needles melting at 136—137°. On analysis it gave the following figures:

0·1349 gave 0·3537 CO_2 and 0·1008 H_2O. C = 71·5; H = 8·3.

This result agrees best with the formula $C_{10}H_{14}O_2$ (C = 72·3; H = 8·4 per cent.), but owing to the very poor yield of this acid it was not found possible to determine its constitution.

Fraction C on hydrolysis gave a viscous oil smelling strongly of fatty acids. It could not be obtained crystalline, and was not further investigated.

II. trans-*Caronic Acid.*

The method adopted for the preparation of *trans*-caronic acid from *d*-carene was identical with that used by Baeyer and Ipatiev (*loc. cit.*) for the preparation of this acid from carone. The oily mixture of acids obtained from the oxidation (no trace of the *cis*-acid could be detected) was converted into the ammonium salt when after concentration the ammonium hydrogen salt of *trans*-caronic acid separated. This was recrystallised from a little water, in which it was only sparingly soluble when it was obtained in small

prisms. The free acid was purified by crystallisation from hot water, when it separated in prisms melting at 212—213°. This acid possessed all the properties ascribed to *trans*-caronic acid, and the melting point was not depressed on admixture with a specimen of *trans*-caronic acid specially prepared for comparison.

The silver salt was obtained as a crystalline precipitate (Found, Ag = 57·7. $C_7H_8O_4Ag_2$ requires Ag = 58·1 per cent.).

d-*Longifolene.*

The fraction of the original oil boiling at 149—151°/36 mm. was repeatedly distilled over sodium, when the sesquiterpene d-*longifolene* was obtained as a colourless, somewhat viscous oil with a faint and not unpleasant odour. It distilled at 254—256°/706 mm., 150—151°/36 mm., and had the following constants: D_{30}^{30} 0·9284, n_D^{30} 1·495, M = 64·15, α_D + 42·73°.

d-Longifolene does not yield a solid nitrosochloride, nitrosate, or nitrosite.

The *hydrochloride* was best prepared by saturating an ethereal solution of the hydrocarbon with hydrogen chloride and allowing it to remain overnight. On removing the ether under diminished pressure, the hydrochloride separated as a crystalline solid which crystallised from methyl alcohol in long prisms or prismatic needles melting at 59—60° and having, in chloroform solution, $[\alpha]_D$ + 7·1°:

0·1866 gave 0·1109 AgCl. Cl = 14·7.

$C_{15}H_{25}Cl$ requires Cl = 14·7 per cent.

The *hydrobromide* was best prepared by dissolving the terpene in an acetic acid solution of hydrogen bromide (saturated at 0°) when, on keeping, the hydrobromide separated in prisms which after crystallisation from alcohol melted at 69—70°:

0·1672 gave 0·111 AgBr. Br = 28·2.

$C_{15}H_{25}Br$ requires Br = 28·0 per cent.

The *hydriodide* which was prepared in a similar manner to the hydrobromide crystallised from alcohol in magnificent prismatic needles which melted at 71°:

0·119 gave 0·0838 AgI. I = 38·2.

$C_{15}H_{25}I$ requires I = 38·0 per cent.

In conclusion, the author wishes to thank his assistant, Mr. T. P. Ghose, for help in the experimental work, and Mr. M. Gopal Rau for many of the analyses and for kindly undertaking the preparation of the dimethylmalonic acid and *trans*-caronic acid required for the purpose of comparison.

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LXII.—*The Cyanine Dyes. Part I. The Constitution of the* iso*Cyanines.*

By WILLIAM HOBSON MILLS and ROBERT SCOTT WISHART.

THE *iso*cyanines were discovered in 1883 by Spalteholz (*Ber.*, 1883, **16**, 1847), and independently by Hoogewerff and van Dorp (*Rec. trav. chim.*, 1883, **2**, 41; 1884, **3**, 344). These investigators found that a purplish-red dye forming magnificent, lustrous green crystals could be obtained from a mixture of the ethiodides of quinaldine and quinoline by the action of potassium hydroxide. Hoogewerff and van Dorp assigned to it the formula $C_{23}H_{23}N_2I$—that is to say, they regarded it as formed by the condensation of one molecule of quinaldine ethiodide with one of quinoline ethiodide with the elimination of hydrogen iodide and of two atoms of hydrogen,

$$C_{12}H_{14}NI + C_{11}H_{12}NI = C_{23}H_{23}N_2I + HI + 2H.$$

Since the compound thus corresponded in composition as well as in general properties with the well known blue dye cyanine, discovered by Greville Williams, similarly formed from the alkyl-iodides of lepidine and quinoline, Hoogewerff and van Dorp named it diethyl*iso*cyanine iodide. Spalteholz formulated the dye as $C_{23}H_{25}N_2I$.

Interest was again aroused in the *iso*cyanines when their value as photographic sensitisers became recognised (Miethe and Traube, *Chem. Ind.*, 1903, **26**, 54).

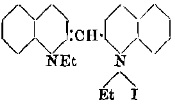
The first suggestion as to the constitution of this class of dyes was made by Decker (*Ber.*, 1891, **24**, 692). Having discovered the alkylquinolinium pseudo-bases (*loc. cit.* and *Ber.*, 1892, **25**, 3326), he saw in them the reactive intermediate products to which the formation of the dyes of the cyanine type was due, and accordingly he expressed the view that the cyanines were the product of the interaction of one molecule of unchanged alkyl-iodide with one molecule of 1-alkyl-2-quinolone arising from the oxidation of the pseudo-base. The idea that the quinolinium pseudo-bases play a principal part in the production of these dyes forms the basis of all the formulæ which have been proposed for the *iso*cyanines.

Another point on which there has been general agreement is that the 2-methyl group of the quinaldine alkyl-iodide is concerned in the condensation. This question has been dealt with especially by Vongerichten and Höfchen (*Ber.*, 1908, **41**, 3054). These investigators showed in the first place that quinaldine alkyl-iodides in which the hydrogen atoms of this methyl group are substituted, as benzylidenequinaldine ethiodide or 2-*iso*propylquinoline meth-

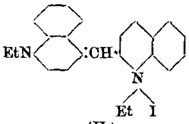
iodide, are incapable of taking part in the formation of *iso*cyanines. It should, however, be pointed out that evidence of this nature, which has been used to a considerable extent in the discussion of the constitution of these dyes, is not altogether conclusive, since the *iso*cyanine condensation is very subject to steric hindrance. Quinoline alkyl-iodides, for example, are prevented from taking part in this condensation by substitution, not only in the 4-position (Miethe and Book, *Ber.*, 1904, **37**, 2823; Kaufmann and Vonderwahl, *Ber.* 1912, **45**, 1404), but also as experiments of Miss F. M. Hamer and Mr. W. K. Braunholtz in this laboratory have shown, in the 5-position, and, according to the patent literature, in the 8-position.

Vongerichten and Höfchen (*loc. cit.*) also showed that 1-ethyl-2-quinolone is formed when diethyl*iso*cyanine chloride is oxidised with alkaline potassium ferricyanide. This proves that the nucleus of the quinaldine residue is linked to the rest of the *iso*cyanine molecule through the 2-position, and therefore presumably through the carbon atom of the 2-methyl group.

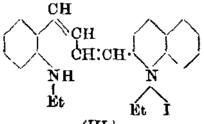
On the assumption that the *iso*cyanines are formed by condensation, through the 2-methyl group, of a quinaldine alkyl-iodide with a quinolinium pseudo-base, with or without concomitant oxidation the three following formulæ have been proposed for diethyl*iso*cyanine iodide:



(I.)



(II.)



(III.)

The first of these is Decker's formula (*J. pr. Chem.*, 1911, [ii], **84** 235). It follows at once from Decker's view of the mechanism of the *iso*cyanine condensation. The second formula was suggested by W. König (*J. pr. Chem.*, 1906, [ii], **73**, 100) as a modification which he regarded on general grounds as more probable, of formula proposed by Miethe and Book (*Ber.*, 1904, **37**, 2008). It differs from Decker's formula in that it represents the quinoli

residue as linked to the rest of the molecule through the 4'- instead of the 2'-position. Very strong evidence that the quinoline residue is actually linked through the 4'-position was obtained by A. Kaufmann and Vonderwahl (*Ber.*, 1912, **45**, 1404). In particular, they showed that quinoline alkyl-iodides substituted with chlorine in the 4-position reacted with quinaldine ethiodide and alkali, with the elimination of hydrogen chloride as well as of hydrogen iodide, to give the same *iso*cyanines as are formed from the corresponding chlorine-free compounds. Their important communication thus affords strong support to König's formula (II). The third formula was also proposed by König. It is based on the view that the pseudo-bases derived from quinoline alkyl-iodides are aldehyde-amines, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CHO$, and represents the *iso*cyanines as the normal condensation products of these with quinaldine alkyl-iodides. This interesting suggestion which, although it had little direct experimental support, could scarcely be proved to be at variance with the facts, will be further considered in a later paper.

Whilst the available evidence must thus be regarded as favouring the second of these three formulæ, it was not of a very direct character, and further information which would assist in furnishing a more secure basis for a constitutional formula for the *iso*cyanines was desirable.

Certain observations had led us to believe that the investigation of the action of potassium permanganate on these dyes would lead to results of interest. We have therefore studied the oxidation by this reagent of 1 : 1-dimethyl*iso*cyanine acetate (the dimethyl compound was selected as being the simplest *iso*cyanine and the acetate because it was the most readily soluble of its salts with common acids), and in the present communication an account is given of the results we have obtained.

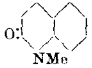
As has already been stated, the oxidation of an *iso*cyanine has previously been investigated by Vongerichten and Höfchen (*loc. cit.*). These authors, using alkaline potassium ferricyanide, isolated a 1-alkylquinolone, and showed that it was derived from the quinaldine half of the molecule, but they were unable to isolate the other products of oxidation.

The oxidation of dimethyl*iso*cyanine acetate with potassium permanganate proceeds very smoothly in ice-cold aqueous solution, and the end of the reaction is sharply marked by the point at which the colour of the gradually added permanganate persists. The quantity of permanganate used corresponds with approximately 3½ atoms of oxygen for one molecule of *iso*cyanine.

From the oxidised solution we were able to isolate 1-methyl-2-quinolone (IV) and, after acidification with hydrochloric acid,

cinchonic acid methochloride (V). (The actual product of the oxidation was probably the corresponding betaine.) The weights of these products, before purification, amounted to approximately 80 and 70 per cent. respectively of those theoretically possible. These two

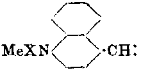
(V.)


(IV.)

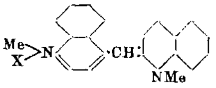
compounds account for all the carbon atoms in the *iso*cyanine, and the two molecules together contain 3 atoms of oxygen. It is clear, *therefore, that 3 atoms of oxygen are required for the oxidation, the half atom or so actually used in excess of this quantity being* consumed in side reactions. Hence the equation for the reaction is:

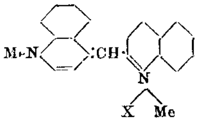
$$C_{21}H_{19}O_3N_2X + 3O = C_{10}H_9ON + C_{11}H_{10}O_2NX.$$

The composition of the products and the number of oxygen atoms used in their formation thus settle the debated question of the number of hydrogen atoms in the molecule of the *iso*cyanine; they show that the view of Hoogewerff and van Dorp that the condensation involves the removal of two atoms of hydrogen by oxidation is correct. At the same time the structural formula of the dye is fixed. For subtraction of the added oxygen atoms from the two products leaves the residues


and

and these on combination give VI as the formula of the *iso*cyanine.


(VI.)


(VII.)

This formula stands in the closest relationship to formula II suggested by König and advocated by Kaufmann and Vonderwahl. In fact, since in each the two nitrogen atoms are connected by a chain of conjugate linkings, it is probable that the two types of formulæ represent virtually tautomeric compounds.

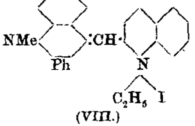
If this should prove to be the case, the objection might perhaps be raised that, whilst the experiments recorded in this paper show

definitely that the dimethyl*iso*cyanine salts have one of the (supposedly) tautomeric formulæ, VI or VII, they do not provide a satisfactory basis for distinguishing between these two. It might be argued that the compound actually oxidised was the *iso*cyanine base set free by the excess of alkali developed by the reduction of the permanganate, especially as the salt employed was that of a weak acid, and that the base might differ in constitution from the salts. The nature of the oxidation products, however, shows that, if they are derived from a base, this must be an ammonium base, not a pseudo-base; and a strong quaternary ammonium base, as this must be, must correspond in constitution with its salts. For if the compounds are tautomeric, as supposed, the acid radicle of the salt and the hydroxyl group of the base must each be attached to the more strongly basic of the two nitrogen atoms.

There is further no apparent reason why a compound of the formula VII, if present, should not be about as readily oxidised to 1-methyl-4-quinolone and a 1-methylquinaldinic acid salt as the substance VI is oxidised to 1-methyl-2-quinolone and a 1-methylcinchonic acid salt. An experiment was carried out in which the quantity of acetic acid necessary to keep the reaction mixture neutral was added to the permanganate solution before it was allowed to run into the *iso*cyanine. The products of oxidation were the same as in weakly alkaline solution and, in spite of careful search, no evidence of the formation of 1-methyl-4-quinolone or of a 1-methyl quaternary salt of quinaldinic acid could be obtained.

It would therefore appear justifiable to draw from these experiments the inference that the dimethyl*iso*cyanine salts have the structure represented by formula VI.

There is an observation of Kaufmann and Vonderwahl which confirms this suggestion of the virtual tautomerism of the *iso*cyanines. These authors have shown (*Ber.*, 1912, **45**, 1418) that 1-ethyl-1′-methyl-2′-phenyl*iso*cyanine iodide (VIII), when heated in a high



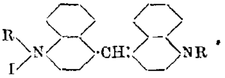
(VIII.)

vacuum, decomposes into ethyl iodide and a base having the composition of a phenylmethylquinolylene-quinaldine. This proves that in this compound the iodine is attached to the nitrogen atom in the quinaldine residue, otherwise methyl iodide would be eliminated.

This substance therefore has the formula VIII, and does not correspond in constitution with the dimethyl*iso*cyanine salts. It is noteworthy that, like other 2′-substituted *iso*cyanines, it is an exceedingly feeble sensitiser (Pope and Mills, *Phot. J.*, 1920, **60**).

If, as would thus appear, the *isocyanines are virtually tautomeric compounds, differences of constitution of this kind would be expected to occur. In the compound* VIII *the basicity of the nitrogen in the quinoline residue must* be lowered by the presence of the adjacent phenyl group, and it is probable that a reversal is thereby brought about of the normal order of basicity of the two nitrogen atoms which obtains in the simpler *iso*cyanines. Thus, whilst the powerfully sensitising 1 : 1′-dimethyl*iso*cyanine salts, and therefore presumably also the closely related 1 : 1′-diethyl- and 1 : 1′ : 6-trimethyl-*iso*cyanine salts have molecular constitutions corresponding with formula VI, certain *iso*cyanines negatively substituted in the quinoline half of the molecule must be regarded as having a structure of the type represented by VII.

The cyanines correspond so closely with the *iso*cyanines in formation, composition, and general properties that it has been generally recognised that their constitution must follow from that of the latter class of dyes. The formula VI established for the *iso*cyanines therefore practically fixes that of the cyanines as



Experimental.

Oxidation of 1 : 1′-*Dimethyl*isocyanine *Acetate.*

Since it was desirable to carry out the oxidation of the *iso*cyanine in aqueous solution, and the chloride, nitrate, and sulphate of the dye were found to be sparingly soluble in water, the more readily soluble acetate was prepared by treating the iodide with silver acetate. 1 : 1′-Dimethyl*iso*cyanine iodide (Pope and Mills, *loc. cit.*) (5 grams) was dissolved in alcohol (250 c.c.), silver acetate (10 grams) ground into a cream with alcohol (30 c.c.) was added, and the mixture was boiled for half an hour. The solution, which was then found to be free from iodide, was filtered, and the filtrate was evaporated to dryness, the last traces of alcohol being carefully removed by a current of warm air. The dimethyl*iso*cyanine acetate obtained in this way was dissolved in water (250 c.c.), and this solution was used for the oxidation. It was browner than true

solutions of dimethyl*iso*cyanine salts, and was possibly a colloidal solution, since the addition of a little acetone immediately restored the brilliant *iso*cyanine colour, and dilution with water had the same effect.

To carry out the oxidation the aqueous solution of the acetate was cooled to 0° and a 3 per cent. solution of potassium permanganate was allowed to drop slowly into the rapidly stirred liquid until a drop placed on filter paper showed the first signs of a permanganate-coloured ring round the moistened spot. In an experiment in which the acetate from 1·74 grams of iodide was dissolved in 100 c.c. of water and oxidised in this manner, 45·7 c.c. of 3 per cent. potassium permanganate solution were required. Since the molecular weight of the iodide, which contains one molecule of methyl alcohol of crystallisation, is 458, the permanganate used corresponds with 3·42 atoms of oxygen per molecule of *iso*cyanine. In most of our later experiments the acetate solution prepared from 5 grams of iodide was divided into two equal parts, and to each of these 67·5 c.c. of a 3 per cent. potassium permanganate solution, corresponding with 3·55 atoms of oxygen per molecule of *iso*cyanine, was added.

Isolation of 1-*Methyl*-2-*quinoline*.—After the addition of the permanganate solution was complete, the precipitated manganese dioxide was removed, and the pale brown filtrate was extracted with chloroform. The chloroform solution, after being dried with potassium carbonate, was evaporated; the brown residue, placed in a vacuum desiccator over solid paraffin and sulphuric acid, became solid after some days. Extraction of the residue with light petroleum (b. p. 40—60°) gave a pale yellow solution, which, on cooling, deposited a substance crystallising in long, colourless needles. After recrystallisation from light petroleum, this substance melted at 73—74°, which is the melting point of 1-methyl-2-quinolone (Knorr and Rabe, *Ber.*, 1897, **30**, 930). The analytical results agreed with those required for this compound. (Found, C = 75·75; H = 5·7. $C_{10}H_9ON$ requires C = 75·43; H = 5·7 per cent.)

The hydrochloride obtained by treating the quinolone with hydrochloric acid melted at 110—113° and the mercurichloride at 189°. The melting points recorded for these compounds are 112° and 189° (Ostermayer, *Ber.*, 1885, **18**, 595; Friedländer and Müller, *Ber.*, 1887, **20**, 2010).

A specimen of 1-methyl-2-quinolone was then prepared from quinoline methiodide by oxidation with alkaline potassium ferricyanide as described by Decker (*J. pr. Chem.*, 1893, [ii], **47**, 31), and a comparison of this with the compound obtained from the *iso*cyanine and, in particular, the agreement of the mixed melting points of the bases, the hydrochlorides, and the mercurichlorides with those of

the separate substances left no doubt as to the identity of the two compounds. From 5 grams of dimethyl*iso*cyanine iodide 1·38 grams of crude methylquinolone were obtained. This weight is 79—80 per cent. of the theoretical amount.

Isolation of Cinchonic Acid Methochloride.—After the removal of the methylquinolone by extraction with chloroform the weakly alkaline liquid was acidified with hydrochloric acid and boiled for an hour with animal charcoal (5 grams). The nearly colourless filtrate from the charcoal was then evaporated to dryness and the residue extracted with absolute alcohol. The alcoholic extract having been concentrated to a volume of about 7 c.c., two volumes of ether were gradually added, when a flocculent precipitate of cinchonic acid methochloride was formed, which was collected and dried; 1·7 grams were thus obtained from 5 grams of dimethyl*iso*cyanine iodide, a weight which corresponds with 69—70 per cent. of the theoretical amount.

As cinchonic acid methochloride is too soluble to be readily recrystallised, it was converted into the corresponding methiodide and methylbetaine, and the identification of these compounds was effected in the following manner.

Cinchonic Acid Methiodide.—This substance was obtained by adding 1 c.c. of a saturated solution of potassium iodide to a concentrated aqueous solution of the chloride (1·5 grams) slightly acidified with hydrochloric acid. The yellow, crystalline precipitate crystallised from alcohol in fine yellow needles melting at 222°, which is the melting point of cinchonic acid methiodide (H. Meyer, *Monatsh.*, 1903, **24**, 201). A specimen of cinchonic acid methiodide (*b*) was prepared from cinchonic acid as described by H. Meyer (*loc. cit.*), and the synthesised compound was carefully compared with that obtained from dimethyl*iso*cyanine iodide (*a*). Both substances, as well as a mixture of the two, melted at 222°, and both, air-dried under the same conditions, contained practically the same percentage of iodine. (Found, I = (*a*) 37·0, (*b*) 37·3. $C_{11}H_{10}O_2NI,H_2O$ requires I = 38·1 per cent.)

After drying at 110° and 10 mm.: Found, (*a*) C = 41·5, H = 3·5; (*b*) C = 41·5, H = 3·4. $C_{11}H_{10}O_2NI$ requires C = 41·9; H = 3·2 per cent.

Cinchonic Acid Methylbetaine.—The methiodide was converted into the corresponding betaine in the usual manner by treating it in aqueous solution with silver oxide and evaporating the filtrate to dryness over sulphuric acid in a vacuum. The betaine was purified by dissolving in absolute alcohol and precipitating with dry ether, and then formed colourless needles melting and decomposing at

219—221° (*a*). A specimen of cinchonic acid methylbetaine, prepared in exactly the same manner from the synthetic methiodide, melted and decomposed at 222—223° (*b*), and the mixture of the two substances melted at the same temperature. Also close correspondence was shown in the behaviour of the two substances when heated side by side in the same bath, darkening beginning in each case at 170°. Claus (*Annalen*, 1892, **270**, 347) gives the melting point of this compound, which varies somewhat with the rate of heating, as 236° (decomp.), and H. Meyer (*loc. cit.*) as 232° (decomp.). Both specimens of betaine were analysed. (Found, (*a*) C=70·4; H=4·8; (*b*) C=70·6; H=4·85; $C_{11}H_9O_2N$ requires C=70·6; H=4·8 per cent.).

When aqueous solutions of the betaine and picric acid are mixed a picrate is formed, crystallising in long, yellow needles. Specimens of this picrate prepared from the betaine from the *iso*cyanine and from the synthetic betaine both melted at 228°, and the melting point of a mixture showed no depression.

The alcohol–ether solution from which the cinchonic acid methochloride had been precipitated contained a small quantity of another chloride melting at 193—194° and giving a picrate melting at 159—161°. Insufficient of this substance was obtained to allow of its identification. It is, however, quite different from quinaldinic acid methochloride.

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CAMBRIDGE. [*Received, April 15th*, 1920.]

LXIII.—*Experiments on the Preparation of Oximino-derivatives.*

By WILLIAM KERSHAW SLATER.

THE conversion of ketones into oximino-derivatives by the action of alkyl nitrites and mineral acids, in accordance with the general equation

$$R\cdot CO\cdot CH_2\cdot R' + Alk\cdot O\cdot NO = R\cdot CO\cdot C(:NOH)\cdot R' + Alk\cdot OH,$$

appears to have been first carried out almost simultaneously by Claisen (*Ber.*, 1887, **20**, 252) and Sandmeyer (*ibid.*, 639). The method has since been extended to a large variety of ketones, but has proved to be by no means generally applicable.

There is little in the work hitherto published on the subject

which serves to explain the variable yields obtained in different cases, or to make possible a reasonable forecast of the approximate conditions likely to ensure even a partial success in applying the method to a new ketone.

Researches, on which the present author and others have been engaged for some time in these laboratories, have emphasised these defects in our very empirical knowledge of the reaction in question.

Prof. Lapworth suggested that a comparative study of ketones of several different types should be undertaken, special attention being devoted to the influence of the mineral acid catalyst, the nature, concentration, and condition of which were evidently the most important factors in determining the course of the reaction and the yields obtained. The activity of the catalyst is determined by many factors, and not least by the basic character of the solvent. Variations in the activity of the catalyst might have been avoided by working in aqueous solution, but, owing to the well-known depressant effect of water on the catalytic activity of hydrogen chloride, the quantity of catalyst required under these conditions is inconveniently large. In the less basic solvent, ether, the quantity of hydrogen chloride required is very small, but its activity is seriously influenced by traces of water.

Ether has, however, a further advantage in that it can be easily removed from the products, and, in consequence of this property, was adopted as the solvent. The alkyl nitrite employed was methyl nitrite, which the author some years ago had used with considerable success in unpublished researches carried out in conjunction with Prof. Lapworth.

Preparation of Methyl Nitrite.

The methyl nitrite was prepared by dropping sulphuric acid (one part of acid to two of water) on a mixture of methyl alcohol and sodium nitrite in molecular proportions, diluted with its own volume of water. The mixture was heated on a water-bath and the vapour passed through a reflux condenser to retain the methyl alcohol. The methyl nitrite was then passed through a cooled U-tube containing glass wool, and finally through a calcium chloride tube before it entered the absorption apparatus, which consisted of a gas jar fitted with a rubber stopper carrying a short, efficient condenser, a Witt stirrer sealed with light petroleum oil, and two lead tubes, one for methyl nitrite and the other for hydrogen chloride.

Method of carrying out the Reaction.

The ketone under investigation, dissolved in five times its own bulk of ether, was placed in the reaction vessel, the stirrer started, and about 10 c.c. of hydrogen chloride were introduced. The stream of methyl nitrite was allowed to enter, and absorption took place rapidly, the ethereal solution being drawn up the delivery tube if the stream of gas was not maintained constant.

It was found that in order to carry on the reaction, 10 c.c. of hydrogen chloride had to be added every fifteen minutes. This addition appeared to correspond with the rate at which the catalyst was used up.

The reaction was continued until the solution would absorb no more methyl nitrite, which in the average case required from one and a-half to two hours. The oximino-derivative was obtained by evaporating off the ether either in a stream of dry air or by gently heating on the water-bath. The subsequent treatment of the material depends on the individual ketone under investigation.

The reaction was studied for four general classes of ketones.

(1) Aryl·CO·CH_3. Example, acetophenone.
(2) Alkyl·CO·CH_3. Example, acetone.
(3) Alkyl·CO·CH_2·CH_3. Example, methyl ethyl ketone.
(4) Aryl·CO·CH_2·CH_3. Example, propiophenone.

Oximinoacetophenone and Oximinoacetone.

In a considerable number of uniform experiments, 10 grams of acetophenone gave, on evaporating methyl alcohol and ether, 11 grams of oil, and this, after agitation with 10 per cent. sodium hydroxide and ether, was divided into 5·1 grams of unchanged ketone and 4·2 grams of oximinoacetophenone, corresponding with a conversion of about 40 per cent. Halving the concentration of hydrogen chloride led to a 20 per cent. yield, whilst doubling it not only failed to raise the yield above 40 per cent., but led to an increased production of by-products, amongst which is a lachrymatory material. Furthermore, experiments with mixtures of the ketone and its oximino-derivative showed that with a constant concentration of the catalyst action would not proceed after the above maximum had occurred.

The case of acetone exactly resembled that of acetophenone, 6 grams of the oximino-derivative being obtained; the method is not so satisfactory as that of Tschugaev (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466), depending on acetoacetic ester.

Oximinomethyl Ethyl Ketone and Oximinopropiophenone.

These substances represent the second type of compound, in which the reaction proceeds almost to completion. Ten grams of methyl ethyl ketone yielded 13·6 grams of the oximino-derivative, corresponding with a 97 per cent. yield. This oximino-derivative appeared to be much less sensitive to the hydrogen chloride than those previously described.

The case of propiophenone resembled that of methyl ethyl ketone, but the yields were not so satisfactory, owing to the formation of what the author believes to be the corresponding nitroso-derivative. Five grams of propiophenone yielded 6 grams of oil, which, on treatment with 10 per cent. sodium hydroxide and ether, gave a bright bluish-green, ethereal solution. This solution was shaken with anhydrous sodium carbonate, and yielded 4·5 grams of oximinopropiophenone, which corresponds with 75 per cent. of the theoretical.

Ethyl Oximinoacetoacetate.

The application of the method to acetoacetic ester resulted in the formation of the *syn*-oximino-derivative described by Jovitschitsch (*Ber.*, 1895, **28**, 2685).

Five grams of acetoacetic ester yield 6 grams of an oil which consisted almost entirely of ethyl oximinoacetoacetate.

Summary of Results.

As the result of the investigation, it is possible to divide ketones into two general classes, namely, (1) those containing the grouping $R{\cdot}CO{\cdot}CH_3$, and (2) those containing the grouping

$$R{\cdot}CO{\cdot}CH_2{\cdot}CH_3.$$

The oximino-derivatives of the first class appear to be very sensitive to hydrogen chloride, and, consequently, it is advisable in dealing with ketones of this class to reduce the concentration of the catalyst to a minimum.

The oximino-compounds of the second class are much more stable towards hydrogen chloride, and the conceutration of the catalyst can be varied between wide limits without materially influencing the end-product.

It is hoped that these observations may serve as a guide when details for the preparation of an unknown oximino-derivative are required.

ADDENDUM.

The Preparation of Cupferron.

The use of methyl nitrite was tried in the preparation of cupferron (*ammonium salt of N-nitroso-β-phenylhydroxylamine*), and was attended by excellent results, as the following example will indicate.

Ten grams of crude phenylhydroxylamine, prepared by Marvel and Kamm's method (*J. Amer. Chem. Soc.*, 1919, **41**, 276), were dissolved in ether, and the sodium chloride present in the crude material was filtered off (1 gram). The ethereal solution was first saturated with dry ammonia, and then, whilst the stream of ammonia was continued, a stream of methyl nitrite was led through. After a few minutes, a mass of lustrous plates began to separate, and at the end of twenty minutes the reaction was complete. The cupferron was collected, washed with a little ether, and dried. The yield was 12 grams, which is equal to 94 per cent. of the theoretical. The material obtained gave the characteristic reactions with copper and iron.

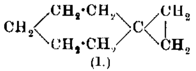
In conclusion, the author wishes to acknowledge his thanks to Prof. Lapworth for the assistance and advice which he has kindly given during the progress of the research.

THE UNIVERSITY,
MANCHESTER. [*Received, March 26th*, 1920.]

LXIV.—*The Formation and Stability of Associated Alicyclic Systems. Part I. A System of Nomenclature, and Some Derivatives of Methane*-II-cyclo*propane and of Methane*-III-cyclo*propane.*

By RICHARD MOORE BEESLEY and JOCELYN FIELD THORPE.

IN a series of papers entitled "The Formation and Stability of *spiro*-Compounds," of which Part II (T., 1919, **115**, 320) has recently been published, we propose to study the reactions of those typical substances, known as *spiro*-compounds, which have one carbon atom common to two ring systems as, for example, in the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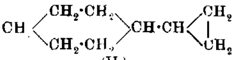
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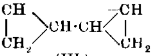
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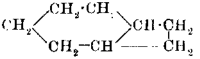
compound I. In the present series it is proposed to investigate the properties of associated ring complexes, of which compounds II, III, and IV can be regarded as typical examples. It is desirable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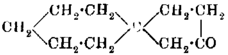

(V.)

to retain this distinction, because the *spiro*-compounds are, in their properties and reactions, quite different from ordinary ring compounds, and because they do not lend themselves to classification in accordance with the system of nomenclature which we are about to propose. Moreover, the present system for naming *spiro*-compounds is quite satisfactory, as is shown by the name 5-*cyclo*hexane-*spirocyclo*pentan-3-one, which adequately represents a compound of formula V.*

It is in the case of associated ring compounds that a really comprehensive system of nomenclature is required, because the only proposals which have hitherto been brought forward do not seem to be entirely satisfactory. Thus Baeyer (*Ber.*, 1900, **33**, 3771) has published a system in which dicyclic systems are considered. Baeyer's method depends on the fact that all dicyclic systems contain three bridged rings which render the compounds capable of being distinguished by the prefixes (0.1.2), (1.2.3), (0.1.4), and so forth, depending on whether the bridge is formed by the linking of two tertiary carbon atoms (0) or whether it is itself formed by 1, 2, or more carbon atoms (compare T., 1901, **79**, 731). This system is without doubt entirely satisfactory so far as dicyclic compounds are

* If thought desirable, the *spiro*-compounds can be included in the new system proposed. For example, compound (V) would be 3-ketobutane-$^{1:4}$II$^{1:1}$-*cyclo*hexane. In fact, the *spiro*-structure would always be indicated by the repetition of the same index figure on the ring side of the Roman numeral.

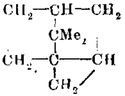
concerned, and, although Baeyer states in the last paragraph of his paper that it is also applicable to tricyclic systems, it is difficult to see how it can be extended without becoming extremely complex. Other suggestions have been made by Borsche (*Annalen*, 1910, **377**, 70) and by Bredt and Savelsberg (*J. pr. Chem.*, 1918, [ii], **97**, 1), but the systems proposed by them are open to two real objections, namely, that terms such as methylene are used to denote ring-formation and not unsaturation, and that the names of the compounds do not provide any indication of the cyclic systems to which they belong. For example, the names proposed for pinene are:

Borsche. 1-Methyl-$\Gamma^{2(4)}$-dimethylmethylene-$\Delta^{1(6)}$-*cyclo*hexene.

Bredt and *Savelsberg.* *m-meso*Methylene-4 : 4 : 2^{β}-trimethyl*cyclo*-$\Delta^{1, 2\beta}$-hexene.

The name in accordance with the nomenclature proposed in this paper would be dimethylmethane-$II^{1:3}$-4-methyl-Δ^4-*cyclo*hexene, indicating that the unsaturated grouping is in the *cyclo*hexane ring, and that the compound belongs to a dicyclic system (II). It is evident, moreover, that the use of the word "meso," which has another and totally different meaning, is an added objection to the system proposed by Bredt and Savelsberg.

A still more complex example may be given in the case of the hydrocarbon,

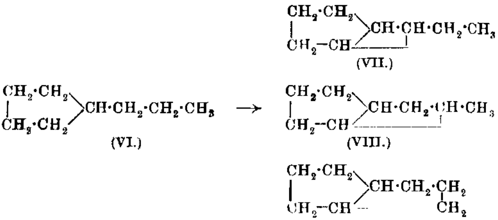


which Bredt and Savelsberg propose to call *p-meso*methylene-1 : 1-dimethyl*cyclo*hexane-*amphi*-2^{α} : 3^{α}-methylene, but would, by our system, be named methane-$II^{1:2}$-*cyclo*hexane-$^{1:4}$II-dimethylmethane.

The system now proposed by us appears to be capable of indefinite extension to alicyclic compounds containing any number of associated rings. It may be briefly outlined as follows:

A compound containing associated rings may be of two kinds.

(**A**) It may be formed from a simple ring compound having a side-chain of carbon atoms from which another ring is produced by a linking between another carbon atom of the ring and another of the side-chain, thus:



(VI.) (VII.) (VIII.) (IX.)

In these cases the side-chain and the ring would be given their usual names, the number of linkings joining the two would be indicated by a Roman numeral and the carbon atoms of the two series participating in the ring complex would be indicated by means of index figures written at the side of the numeral on which the particular residue is placed. In this way:

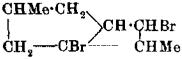
(VII) is Ethylmethane-II$^{1:2}$-*cyclo*pentane.*

(VIII) is 2-Methylethane-$^{1:2}$II$^{1:2}$-*cyclo*pentane.

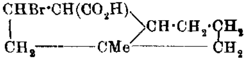
(IX) is Propane-$^{1:3}$II$^{1:2}$-*cyclo*pentane.

It is evident that under this scheme compound VI would be propane-^{1}I^{1}-*cyclo*pentane, but as this hydrocarbon does not contain associated rings there is no need to alter the existing nomenclature of the type, that is, for example, *n*-propyl*cyclo*pentane.

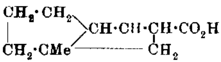
The naming of derivatives would then follow in the ordinary way, the groups in each portion being treated as at present; thus (*A*) is



(*A*.)



(*B*.)



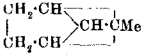
(*C*.)

1-bromo-2-methylethane-$^{1:2}$II$^{1:2}$-2-bromo-4-methyl*cyclo*pentane, (*B*) is propane-$^{1:3}$II$^{1:2}$-4-bromo-2-methyl*cyclo*pentane-5-carboxylic acid, and (*C*) is 2-carboxypropane-$^{1:3}$-II$^{1:2}$-2-methyl*cyclo*pentane. It will be noticed that the index figures, taken in order on either side

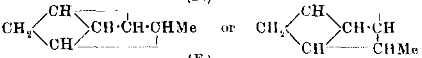
* In the case of methane derivatives it is unnecessary to show index figures on the methane side of the Roman numeral as the linkings can only emerge from one carbon atom.

of the Roman numeral, show, in each case, the actual carbon atoms linked.

If a second, third, or *n*-th ring is formed by the linking of more carbon atoms of the original ring and side-chain, the procedure is the same; thus, (*D*) is methylmethane-III$^{1:2:5}$-*cyclo*pentane, (*E*) is

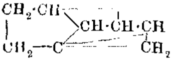


(*D*.)

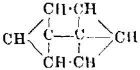


(*E*.)

2-methylethane-$^{1:1:2}$-III$^{1:2:4}$-*cyclo*butane, (*F*) is propane-$^{1:1:2:3}$IV$^{1:5:2:2}$-*cyclo*pentane, and (*G*) is ethane-$^{1:1:1:2:2:2}$VI-$^{1:2:3:4:5:6}$-*cyclo*hexane.



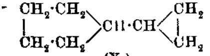
(*F*.)



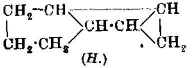
(*G*.)

It is true that this system of nomenclature could be simplified and still rendered quite intelligible by omitting the Roman numeral and leaving the index figures to denote the carbon atoms involved, thus, ethane-$^{(1:2:2)\ (1:2:5)}$-*cyclo*pentane, but it is thought that the inclusion of the numeral will make for clearness, especially when derivatives are being named; moreover, the presence of the numeral will at once indicate the class to which the compound belongs. It is also evident that the first index figure, on either side of the Roman numeral, might be omitted, because, since the numbering in each series starts with the linked carbon atoms, this must necessarily be 1 in every case. Here again, however, it is thought that the assistance given to the eye warrants its inclusion.

(B) The associated ring compound may be formed by linking pairs of carbon atoms in a ring to which another ring is already attached, as, for example, in substance (X). Here again the system

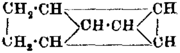


(X.)

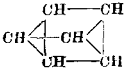


(*H*.)

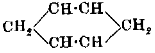
is the same, and (*H*) is *cyclo*propane-$^{1:2}$II$^{1:2}$-*cyclo*pentane, (*J*) is



(*J*.)



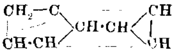
(*K*.)



(XI.)

*cyclo*propane-$^{1:2:3}$III$^{1:2:5}$-*cyclo*pentane, (*K*) is *cyclo*propane-$^{1:2:3}$ III$^{1:2:3}$-*cyclo*propane, and (XI) is *cyclo*propane-$^{1:3}$II$^{1:2}$-*cyclo* propane, the nomenclature of derivatives being the same as alread illustrated under class (**A**).

It may happen that a compound can be assigned to both class (**A** and class (**B**), but no difficulties present themselves in such case for example, (XII) is methane-II$^{3:4}$-*cyclo*butane-$^{1:2:4}$III$^{1:2:}$



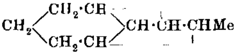
(XII.)

(XIII.)

*cyclo*propane, and (XIII) is ethane-$^{1:2}$II$^{2:3}$-*cyclo*propane-$^{1:2:3}$II $^{1:2:3}$-*cyclo*propane.

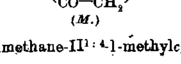
It will be noticed that compound X (p. 595) would be calle under the system proposed, *cyclo*propane-^{1}I^{1}-*cyclo*pentane, and no as at present, *cyclo*propyl*cyclo*pentane. As in this case two ass ciated rings are present, it is probably desirable to adopt the ne method of nomenclature.

Regarding the rules to be observed when naming a compoun little ambiguity can exist in connexion with those substances whic fall within class (**A**). These compounds form dicyclic systems whe two linkings couple the side-chain and the ring, and tricyclic, tetr cyclic systems, and so forth, when three, four, or more carbon atom are linked together. The only rules which appear to be necessar are: (1) That one of the linked carbon atoms in the riug should b called 1, and that the corresponding carbon atom in the cha should be also called 1. The numbering would then proceed i the ring clockwise, and in the side-chain in the usual manne (2) That the name of the simplest portion of the chain entering int ring formation should be used first, and any attached groups shoul be named as derivatives of the simplest chain; thus, (*L*) would b

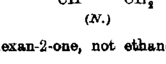


(*L.*)

2-methylethane-$^{1:2}$III$^{1:2:6}$-*cyclo*hexane, and not propane-$^{1:2}$III $^{1:2:6}$-*cyclo*hexane, or, to take two typical examples, (*M*) would b



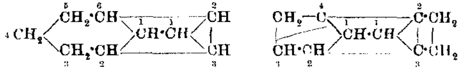
(*M.*)



(*N.*)

dimethylmethane-II$^{1:4}$-1-methyl*cyclo*hexan-2-one, not ethane-$^{1:2}$II

$^{1:3}$-2 : 2 : 3-trimethyl*cyclo*pentan-4-one, and (*N*) would be dimethyl-methane-II$^{1:2}$-*cyclo*butane-2-carboxylic acid, and not ethane-$^{1:2}$II$^{1:3}$-2 : 2-dimethyl*cyclo*propane-3-carboxylic acid. With those compounds falling within class (**B**), the rules are the same. Thus the simplest ring should always be taken first, and the numbering should start from two linked carbon atoms, one in each ring, and proceed clockwise, thus, (*O*) should be *cyclo*propane-$^{1:2:3}$III$^{1:2:6}$-

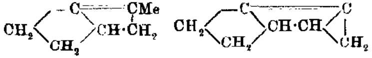


(*O*.) (*P*.)

*cyclo*hexane, and not *cyclo*hexane-$^{1:2:6}$III$^{1:2:3}$-*cyclo*propane. When naming a new compound, the first point to ascertain is whether it falls within class (**A**) or class (**B**), or whether it is made up of both these types. If the latter, the system should be analysed, and the name should start with the simplest system belonging to class (**A**) involved, as in examples (XII) and (XIII) on page 596. In some highly complex cases it will again be necessary to bring in class (**A**) at the end of the name, as, for example, in the compound (*P*), in which both ends belong to class (**A**) and the middle portion to class (**B**); the name of this substance would be methane-II$^{3:4}$-*cyclo*butane-$^{1:2:4}$III$^{1:3:2}$-*cyclo*-propane-$^{2:3}$II$^{1:2}$-ethane.

In some cases it will happen that a substance, whilst capable of being assigned to a single class, that is, to either (**A**) or (**B**), can also be derived from the mixed type composed of both (**A**) and (**B**). Such is the case with the compound (XI) on page 595, which can equally well be named methane-II$^{3:4}$-*cyclo*butane-$^{1:2}$II-methane. The rule should always be, however, to assign a substance to a single class, if possible, rather than to introduce the mixed type.

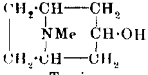
A system such as that outlined above seems to serve as a ready means for naming substances having associated rings, many of which are certain to be made and studied in the near future. It should be pointed out, in passing, that where double linkings occur between two carbon atoms in the system, the fact will be evident by the occurrence of consecutive recurring figures in the same positions on either side of the Roman numeral; thus, (*Q*) is 2-methylethane-



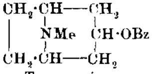
(*Q*.) (*R*.)

$^{1:2:2}$III$^{1:4:4}$-*cyclo*butane, and (*R*) is *cyclo*propane-$^{1:3:3}$III$^{1:2:2}$-*cyclo*propane.

It may be added that the scheme proposed in this paper can also be applied to complex heterocyclic systems; thus, tropine would be

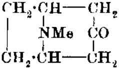


Tropine.

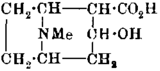


Tropacocaine.

methylamine-II$^{1:5}$-3-hydroxy*cyclo*heptane, tropacocaine would be

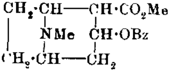


Tropinone.

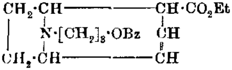


Ecgonine.

methylamine-II$^{1:5}$-3-benzoyl*cyclo*heptane, tropinone would be



Cocaine.

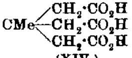


Eccaine.

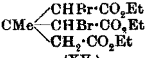
methylamine-II$^{1:5}$-*cyclo*heptan-3-one, ecgonine would be methylamine-II$^{1:5}$-*cyclo*heptan-3-ol-2-carboxylic acid, cocaine would be methyl methylamine-II$^{1:5}$-3-benzoyl*cyclo*heptane-4-carboxylate, and eccaine, ethyl γ-benzoylpropylamine-II$^{1:5}$-Δ^3-*cyclo*heptene-2-carboxylate.

We have been led to propose this system of nomenclature in order to name certain compounds, belonging to two of the simpler series of associated rings, which are described in this paper, and for which no adequate system of nomenclature exists. A brief mention of one of these compounds was made in the *Proceedings* (1913, **29**, 346), but the war and the necessity for preparing considerable quantities of material has delayed publication until now.

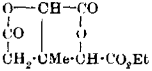
The starting point is ββ-dimethylpropanetricarboxylic acid (XIV) (Thorpe and Wood, T., 1913, **103**, 1583), which can be converted into the dibromo-ethyl ester (XV) on treatment with bromine and phosphorus pentabromide under special conditions described in the experimental part. If this bromo-ester is treated with pyridine it is converted into the di-lactone ester (XVI), from which the acid (XVII) can be obtained on hydrolysis.

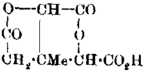


(XIV.)

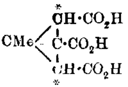


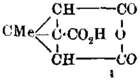
(XV.)


(XVI.)

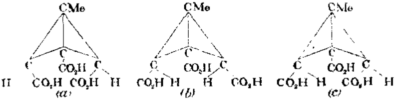

(XVII.)

If, however, the bromo-ester (XV) is treated with concentrated aqueous potassium hydroxide at a high temperature it is converted into the acid (XVIII), for which the name carboxymethane-II$^{1:3}$-3-methyl*cyclo*propane-1:2-dicarboxylic acid is proposed. This acid


(XVIII.)


(XIX.)

is a remarkable substance, and is, we believe, the first of its type to be prepared. It contains two asymmetric carbon atoms, marked above with asterisks, and should, therefore, exist in *cis*- and *trans*-forms corresponding with the two inactive forms of tartaric acid. On the other hand, there is no possibility of free rotation about these two carbon atoms owing to their participation in the double-ring formation. The acid should, therefore, also exist in two forms corresponding with fumaric and maleic acids. An examination of the following figures shows, however, that three inactive forms only are theoretically possible:



One of these, that represented by Fig. *a*, might be expected to give an anhydro-acid with great readiness,† and, of the other two, that represented by Fig. *c* might also be expected to give an anhydro-acid, but with less readiness than the acid of Fig. *a*. The acid of Fig. *c* is, as a matter of fact, similar in structure to *cis*-norpinic acid which, as Perkin and Simonsen have shown (T., 1909, **95**, 1176), is converted into the anhydride when heated in a sealed tube with acetic anhydride at 220°. On the other hand, the acid

* The fourth possible form in the mirror image of Fig. c.

† The two asymmetric carbon atoms are evidently brought into close proximity by the closing of the second *cyclo*propane ring. This fact, which can be easily demonstrated on the models, is well illustrated by the experiments described in this paper (see note by C. K. Ingold, p. 603).

represented by Fig. *b* should not give an anhydro-acid unless the carboxyl group attached to one of the asymmetric carbon atoms entered into combination with the carboxyl group attached to the tertiary carbon atom at the far angle of the system, a contingency which, as will be shown later, is extremely unlikely because the tribasic acid (XXVIII) (p. 602), in which the third ring is formed, shows no tendency to pass into an anhydro-acid. We have therefore assigned the formula XIX to both the anhydro-acids which we have prepared.

The acid of formula XVIII can, as a matter of fact, be isolated in three distinct modifications, melting at 193°, 165°, and at 154° respectively. The acid melting at 154° passes into the anhydro-acid melting at 103° when it is heated a few degrees above its melting point. It therefore, in all probability, has a strncture represented by Fig. *a*. The acid melting at 165° also gives an anhydro-acid (melting at 121°), bnt only does so when it is heated in a sealed tube with acetic anhydride at 200°. The acid has therefore the structure shown in Fig. *c*. Finally, the acid melting at 193°, which shows no tendency whatever to yield an anhydro-acid, in all probability has the structure given in Fig. *b*.

The anhydro-acids are each converted into the acids, from which they are derived, on boiling with water, but we have not as yet succeeded in finding the conditions under which the three acids are converted the one into the other. This is probably in part due to the fact that one cannot subject the acids to the usual conditions which convert *cis*- into *trans*-forms, such as prolonged heating with hydrochloric acid or hydrobromic acid in a sealed tube, because under these conditions all three modifications are transformed into the di-lactonic acid (XVII), a fact which clearly shows that the structures assigned to them by us are correct. There may, however, be some fundamental reason why the interconversion of these three forms is impossible, because it will be noticed that, in an acid of formula XVIII, the ring must be broken before free rotation, a condition which is presumably necessary for interconversion, can ensue, and since it is evident that the lactone form is more stable than the ring complex, it follows that all attempts to bring about interconversion of the three forms will lead to the fission of the carbon ring systems.

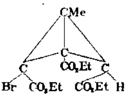
As it happens, the three acids are all produced in the original reaction and in, so far as we can judge, about equal proportions. Their separation is a simple matter because the acids themselves are insoluble in dry ether, whereas the anhydro-acids are readily soluble in this solvent. It is only necessary, therefore, to heat the mixed acids, extract the anhydro-acid of the acid melting at 154°,

then to treat the residue with acetic anhydride, and, after extracting the anhydro-acid of the acid melting at 165°, to leave the acid melting at 193° in a comparatively pure condition.*

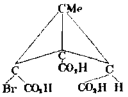
It follows from the fact described above that an acid of formula XVIII, although containing only two asymmetric carbon atoms, can exist in three inactive forms. The mirror images of two of these forms, namely, those represented by Figs. *a* and *b*, that is to say, the acids melting at 193° and 154° respectively, are superimposable. They are therefore not resolvable. On the other hand, the mirror images of the acid represented by Fig. *c* are not superimposable, and this acid, which is that melting at 165°, is probably capable of resolution in its optical enantiomorphs. As regards their general behaviour, the three acids are comparatively stable substances. They do not, for example, reduce alkaline permanganate in the cold and do not decolorise bromine.

Except when heated in a sealed tube with either concentrated hydrochloric or hydrobromic acids, when they are converted, as already mentioned, into the di-lactonic acid (XVII), they remain unaltered even after prolonged boiling with aqueous acids or alkalis.

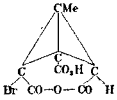
A very remarkable confirmation of the correctness of the formulæ assigned to these acids by us is afforded by a study of their behaviour on bromination. When, for example, the acid melting at 154° is treated with the right quantity of phosphorus pentabromide and bromine to form the monobromo-acid bromide and the product is poured into alcohol, the bromo-ester (XXI) is obtained.



(XXI.)



(XXII.)



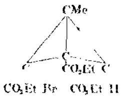
(XXIII.)

This bromo-ester is not altered by boiling pyridine, and when hydrolysed by alkali hydroxide yields the bromo-acid (XXII). The bromine atom in this compound is extremely unreactive, and is not attacked by any of the usual reagents, although the acid is readily converted into the anhydro-acid (XXIII) on treatment with acetyl chloride.

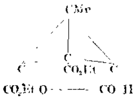
The acid melting at 165°, when treated in the same way, is con-

* We propose to name the acid melting at 154° the *meso-cis*-acid, that melting at 193° the *meso-trans*-acid, and that melting at 165° the racemic acid.

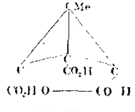
verted into a similar bromo-ester (XXIV), which, when boiled wi pyridine, passes into the lactonic ethyl ester (XXV), from whi the lactonic acid (XXVI) can be prepared on hydrolysis.



(XXIV.)

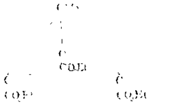


(XXV.)

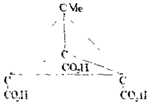


(XXVI.)

When the acid melting at 193° is treated with phosphorus pe bromide and bromine, and the product is poured into alcohol, oil is obtained which is free from bromine. This oil is evidently compound XXVII, since it yields the acid (XXVIII) on hyc lysis.

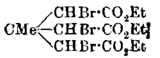


(XXVII.)

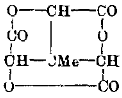


(XXVIII.)

The acid (XXVIII), for which we propose the name met methane-III$^{1:2:3}$-*cyclo*propane-1:2:3-tricarboxylic acid, is ident with that already briefly mentioned in the *Proceedings* (*loc. c* It is also formed, but only in small quantities, when ββ-dimet propanetricarboxylic acid (XIV) is converted into its tribromo-e ester (XXIX), and this is treated with concentrated aqueous al hydroxide at a high temperature. When boiled with pyridine, tribromo-ester is converted into the tri-lactone (XXX) (m. p. 18



(XXIX.)



(XXX.)

Methylmethane-III$^{1:2:3}$-*cyclo*propane-1:2:3-tricarboxylic could be isolated in only one form. It does not yield an anhy acid even when heated with acetic anhydride at a high temperat It does not reduce alkaline permanganate in the cold, but is oxid on heating, yielding methylsuccinic acid, together with other ducts which were not identified; it does not decolorise bromine

; stable towards boiling acids and alkalis, but when heated in a ealed tube, with either concentrated hydrochloric or hydrobromic cids, it is completely converted into the tri-lactone melting at 206° XXX).

[The following note has been written by Mr. C. K. INGOLD.]

In the paper already mentioned (*loc. cit.*), certain alicyclic ring tructures were examined in the light of the hypothesis that the esultant lines of action of the forces of valency in such carbon ings are not straight lines, but are more or less deeply curved, he amount of curvature being determined by an equilibrium in he distribution of the strains of the ring. In any ring, such as he *cyclo*propane ring represented in Fig. 1, if the whole of the

FIG. 1.

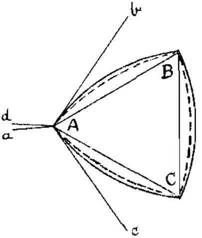
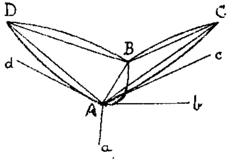


FIG. 2.



istortion were borne by the atoms, the valency resultants would e along the shortest possible paths, the straight lines AB, BC, CA. The pair of valencies AB, AC, for example, would in this ase emerge from the carbon atom A at a considerably smaller nclination than do the corresponding unstrained directions Ab, Ac. If, on the other hand, the whole of the distortion resided on he valencies, so that the directions of emergence from each carbon tom were the unstrained directions Ab, Ac, etc., inclined to one nother at the normal tetrahedral angle ($2\cos^{-1}\frac{1}{3}\sqrt{3} = 109°28'16''$), he valency resultants themselves would pursue paths of maximum urvature the terminal tangents of which are the unstrained direcions in question. Previous experiments have indicated (T., 1919, **15**, 323) that the distortion lies neither wholly on the atoms or wholly on the valencies, but partly on both, in which case the rue paths of the valency resultants must be curves, such as the

dotted lines in Fig. 1 are drawn to represent, lying between the limiting straight paths on the one hand and the paths of maximum possible curvature on the other. The terminal tangents of these true (dotted) paths will therefore be inclined at each carbon atom at some angle intermediate between 60° and $2\cos^{-1}\frac{1}{3}\sqrt{3}$.

In any simple carbon ring such as the above, it is clear, both from symmetry and from the mechanical equilibrium of the carbon atoms, that all the limiting curved paths must lie in the same plane with the straight paths. The consideration of a more complex system, such as the *dicyclo*butane ring (Fig. 2), is, on the other hand, complicated by the fact that the limiting straight paths AB, BC, CA, BD, DA lie in two planes, and the limiting curved paths in three. The curved paths AC, BC, for example, will, from the mechanical equilibrium of the carbon atom, C, lie in the plane ABC. For similar reasons, the curved paths AD, BD will lie in the plane ABD. Both symmetry and the mechanical equilibrium of the carbon atoms A and B require that the curved path AB shall occupy a plane which bisects the angle between the planes of the two component *cyclo*propane rings ABC and ABD.

It is of considerable interest to calculate the angle at which the planes of the two *cyclo*propane rings are inclined. To do this, we have to consider in turn the two limiting conditions imposed by the equilibrium in the strain distribution.

Take, first, the case in which all the valency paths are straight. The carbon atom A will have its four valencies emanating in the directions Aa, AB, AC, AD. In accordance with a hypothesis which was made the subject of a previous communication (T., 1915, **107**, 1080), these four directions will set themselves in such a way that, whilst the angle BAC is 60° and the angle BAD is 60°, the angles between every other pair of valencies (namely, the angles aAB, aAC, aAD, and CAD) will be equal. Describe a sphere round A as centre, and let the lines Aa, AB, AC, AD cut it at a', B', C', D', respectively. Joining these points by arcs of great circles, we obtain the series of spherical triangles represented in Fig. 3, in which the sides $B'C'$ and $B'D'$ are each 60°, whilst the sides $a'A'$, $a'C'$, $a'D'$, $C'D'$ are all equal, say, to 2θ. The angle at B' of the spherical triangle $C'B'D'$ is the angle between the planes ABC and ABD, that is to say, it is the angle, 2ϕ, which it is intended to calculate.

From the spherical triangle $a'B'C'$ we have

$$\cos(180° - \phi) = \frac{(1 - \cos 60°) \cdot \cos 2\theta}{\sin 60° \cdot \sin 2\theta},$$

and from the spherical triangle $C'B'D'$,

$$\cos 2\phi = \frac{\cos 2\theta - \cos^2 60^\circ}{\sin^2 60^\circ}.$$

These equations transform into

$$\frac{\sin\theta}{\sin\phi} = \sin 60^\circ$$

and

$$\frac{\cot 2\theta}{\cos\phi} = \frac{\sin 60^\circ}{\cos 60^\circ - 1}.$$

Eliminating from the last two equations the angle ϕ, we obtain a cubic in $\cos 2\theta$,

$$2\cos^3 2\theta + 2\cos^2 2\theta - 2\cos 2\theta - 1 = 0,$$

FIG. 3.

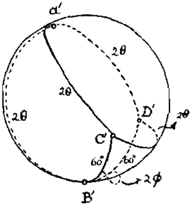
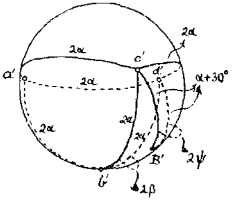


FIG. 4.



the exact solution of which is

$$\cos 2\theta = \frac{1}{3}\left[\left\{\frac{5}{4} + i\sqrt{64 - \frac{25}{16}}\right\}^{\frac{1}{3}} + \left\{\frac{5}{4} - i\sqrt{64 - \frac{25}{16}}\right\}^{\frac{1}{3}} - 1\right],$$

where i is the square root of minus one. This is the irreducible case of Cardan's solution. Extracting the real roots by De Moivre's theorem, we obtain

$$\cos 2\theta = \frac{4}{3}\cos\frac{\xi}{3} - \frac{1}{3},\ \cos 2\theta = \frac{4}{3}\cos\frac{\xi + 2\pi}{3} - \frac{1}{3},\ \cos 2\theta = \frac{4}{3}\cos\frac{\xi + 4\pi}{3} - \frac{1}{3}$$

where

$$\tan\xi = \frac{4}{5}\sqrt{64 - \frac{25}{16}}.$$

The second of these three roots leads to an imaginary value of θ. The first and third correspond with real angles, but the latter alone satisfies the pair of original equations from which the cubic was derived. We therefore have, since $\xi = 81^\circ 0' 39''$, that

$2\theta = 113°46'4''$, and by substitution, $2\phi = 150°32'28''$. The latter angle is the angle between the planes of the two *cyclo*propane rings calculated on the assumption that all the valency resultants follow their limiting straight paths.

Now suppose that all the valency resultants follow their limiting curved paths. The four valencies of the carbon atom A (Fig. 2) will emerge from that atom in the tangential directions Aa, Ab, Ac, Ad, inclined to one another at the normal tetrahedral angle. If we describe a sphere round A as centre and join the points a', b', c', d', in which the lines Aa, Ab, Ac, Ad cut the spherical surface by arcs of great circles, we obtain, as before, a network of spherical triangles (Fig. 4) the sides of which are all equal to $2\alpha = 2\cos^{-1}\frac{1}{3}\sqrt{3}$. If 2β is the angle at b' of the spherical triangle $c'b'd'$, we have, as before,

$$\frac{\sin\alpha}{\sin\beta} = \sin 2\alpha,$$

which, since $\sin\alpha = \dfrac{\sqrt{2}}{\sqrt{3}}$ and $\sin 2\alpha = \dfrac{2}{3}\sqrt{2}$, gives $2\beta = 120°$.

This is the angle between the planes bAc and bAd (Fig. 2). To obtain from it the angle between the planes BAC and BAD, we notice that the plane bAB bisects the angle between the planes bAc and bAd, so that if AB cuts the sphere in B' (Fig. 4), then this point must lie on the median from b' of the spherical triangle $b'c'd'$; also, if B' be joined to c' and d' by arcs of great circles, the angular distances $B'c'$ and $B'd'$ will each be $\alpha + 30°$, which completely defines the position of the point B'. The angle at B' of the spherical triangle $c'B'd'$ is clearly the angle between the planes BAc, BAd, that is to say, it is the required angle between the planes BAC and BAD. If we call the angle in question 2ψ, then from the spherical triangle $c'B'b'$ we have

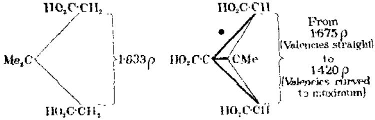
$$\frac{\sin 2\alpha}{\sin(180° - \psi)} = \frac{\sin(\alpha + 30°)}{\sin\beta},$$

in which $\alpha = 2\cos^{-1}\frac{1}{3}\sqrt{3}$ and $\beta = 60°$. Hence $2\psi = 110°9'40''$.

The planes of the *cyclo*propane rings ABC and ABD (Fig. 2) will therefore be inclined at the angle $150°32'28''$ or the angle $110°9'40''$, according as the paths of the valency resultants are quite straight or curved to the maximum, and it is clear that in the latter case the carbon atoms C and D will be nearer together than in the former. In all actual cases, the inclinations of the planes and the distance between the carbon atoms C and D will lie between these limits, the precise values being determined by the strain equilibria.

The actual distance between the carbon atoms *C* and *D* can readily be calculated if we assume that a constant distance separates every pair of carbon atoms in direct combination. Mention has already been made (T., 1919, **115**, 329) of certain experiments which indicate that in condensed alicyclic rings of this kind the distance between two carbon atoms directly combined is constant, or approximately so. Assuming, then, that the distance is constant and equal to ρ, we have that the distance between the carbon atoms *C* and *D* is equal to ρ multiplied by the sine of 60° and by twice the sine of half the angle between the planes of the two *cyclo*propane rings.

It is of interest to compare this distance with the distance between the α and α' carbon atoms of a simple open-chain structure, such as *n*-propane. To take specific cases, we find that the distance between the α- and α'-carbon atoms of $\beta\beta$-dimethylglutaric acid (I) is equal to $2/3 . \sqrt{6} . \rho = 1{\cdot}633\rho$. Directly comparable with this is the distance between the tertiary carbon atoms of methyl*dicyclo*butanetricarboxylic acid (II). This works out to

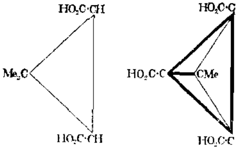


(I.) (II.) (*trans*-form.)

$1{\cdot}675\rho$ on the assumption that the ring-bound valency resultants follow their limiting straight paths, and to $1{\cdot}420\rho$ if we assume that the resultants follow their limiting paths having maximum curvature. If, therefore, the paths of the valency resultants in the *dicyclo*butane acid (II) are straight, or practically so, then the distance between the tertiary carbon atoms should be greater than the distance between the α- and α'-carbon atoms of the glutaric acid (I). It should therefore be distinctly a more difficult matter to establish a bond between the pair of carbon atoms in question in the former compound than in the latter. On the other hand, if the valency paths in the *dicyclo*butane acid have the maximum of curvature, the distance between the carbon atoms will be much less than in the case of the glutaric acid, and it should be very much easier to bridge the *dicyclo*butane acid with the formation of the "caged" acid (IV) than it is to bridge the glutaric acid system to form the *cyclo*propane acid (III).

As a matter of fact, all the experiments described in this paper with the *dicyclo*butane acid (II) point in one direction, namely,

that the tertiary carbon atoms are much closer together than is the case with the α- and α′-carbon atoms of ββ-dimethylglutaric acid. Bridging to form the caged acid (IV) appears to take place



(III.) (IV.)

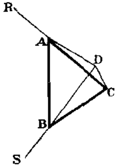
with remarkable readiness, and groups attached to the tertiary carbon atoms, if they are in *cis*-positions, possess a strong tendency to react with each other.

It is clear from what has been said that, in order to explain this result, one has to assume that the paths of the valency resultants in the *dicyclo*butane system have a considerable amount of curvature. We can place a lower limit on what this curvature must be by considering how much curvature would be necessary to give a distance between the tertiary carbon atoms of the *dicyclo*butane acid (II) equal to 1·633ρ, the distance between the α- and α′-carbon atoms of dimethylglutaric acid. Precise mathematical treatment would be lengthy, but an approximate estimate may be obtained if we take the curvatures of the valency paths, reckoned in per cents. of the possible maxima, to be a linear function of the distance between the tertiary carbon atoms. Calculating in this way, one finds that if the valencies of the *dicyclo*butane acid had curvatures equal to 16·5 per cent. of the maximum possible, the tertiary carbon atoms would be just as far apart as the α- and α′-carbon atoms of dimethylglutaric acid. In view of the experimental evidence, we may therefore say that the curvatures are considerably greater than 16·5 per cent. of the theoretical maxima.

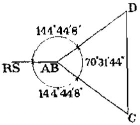
The general inference seems to be that, in agreement with the conclusions reached as a result of certain studies made with *spiro*-compounds (T., 1919, **115**, 322), the paths of the valency resultants in alicyclic rings are distinctly, and often considerably, curved. The present example is one of special interest on account of the fact that we are enabled to place a lower limit on the amount of curvature which actually exists in the constitution of the molecular structure discussed.

Whilst the above considerations lead to an intelligible view of

the experimental results, and have the merit of correlating them with certain previously ascertained facts regarding condensed alicyclic systems, there is another very simple way of looking at the present experimental data which ought not to be lost sight of in the absence of certain knowledge. One of the salient results of the experimental investigation is the great ease with which the *trans-dicyclo*butane acid passes into the "caged" acid. This fact can be strikingly brought out by making a single assumption with regard to the positions of the planes occupied by the valency directions of the carbon atoms at the ends of the bridge-bond of the *dicyclo*butane structure.



(*X.*)

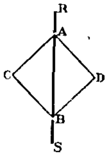


(*Y.*)

Considering, first, the caged structure *ABCD* (formula *X*), let *AR* and *BS* be the directions of the free valencies attached to the carbon atoms *A* and *B*. For the sake of simplicity, we may suppose all valency directions to be straight. Taking a plan-view (formula *Y*) of the structure (that is, the view from some distant point on the projection of *AB*), we obtain three trace-lines, $(AB)(RS)$, $(AB)C$, and $(AB)D$, corresponding with the three planes *ABRS*, *ABC*, and *ABD*. If we assume that a constant distance separates every carbon atom in the "caged" structure from every other, we can show in a few steps that the angle between the planes *ABC* and *ABD*, that is, the angle $C(AB)D$ in formula *Y*, is $\cos^{-1}(\frac{1}{3})$, that is, $70°31'44''$. This means that the angle between each of the other pairs of planes, namely, the angles $(RS)(AB)C$ and $(RS)(AB)D$ are each equal to $144°44'8''$.

Now suppose that the bond *CD* is broken, and suppose that the three planes *ABRS*, *ABC*, and *ABD* maintain the same relative positions. This assumption is clearly the negation of the principle that valencies emerging from a carbon atom will set themselves so that their directions (their initial directions if they are curved) are as evenly distributed in space as possible, for it has already been noticed that the result of applying this principle to the carbon atoms *A* and *B* leads to much higher values for the

angle between the planes *ABC* and *ABD*. One might attempt to justify the assumption, however, by supposing that all carbon atoms, even when not in direct combination, attract one another, and if they are near enough originally (that is, through the structure of the substance) to be within the sphere of one another's influence, this attraction would tend to draw them nearer, and might in the present case be sufficient to prevent the planes *ABC* and *ABD* springing apart to a larger inclination when the bond *CD* is broken. Whether this is so or not, if the hypothesis that the planes *ABRS*, *ABC*, and *ABD* retain the same relative inclinations is tentatively accepted, we have the obvious result that the distance between the carbon atoms *C* and *D* is the same in the *dicyclo*butane structure (formula *Z*) as it is in the "caged" com-



(*Z*)

pound. If this is really the case, it gives particularly clear significance to the remarkable degree of facility with which the "caged" substance was formed.

EXPERIMENTAL.

(1) *The Dibromination of ββ-Dimethylpropanetricarboxylic Acid. Ethyl ββ-Dibromodimethylpropanetricarboxylate* (XV, p. 599).

This bromination can be effected by adding 317 grams of phosphorus pentabromide to 50 grams of the acid contained in a Geissler flask, and then adding 80 grams of bromine gradually down the condenser tube. No bromine should be added until the contents of the flask, after the addition of the phosphorus pentabromide, have become completely liquid, and it should then be dropped into the flask very slowly, the temperature being kept as far as possible in the neighbourhood of 20°. The operation takes some little time, but it is essential to adhere to these conditions, otherwise a product containing the correct amount of bromine will not be obtained. After all the bromine has been added, the mixture may be warmed on the water-bath for half an hour, when it will be found that all free halogen has disappeared. The pro-

duct is then poured slowly into three times its volume of absolute alcohol, the temperature of the solution being kept below 25° throughout the operation. Afterwards, when the alcoholic solution has remained at the ordinary temperature for twelve hours, water is added, the precipitated oil extracted with ether, the ethereal extract thoroughly washed, first with water and then with dilute sodium carbonate solution, and the oily product isolated in the usual way.

The dibromo-ester cannot be distilled without decomposition. When, for example, it is fractionated under diminished pressure, it yields a fraction of constant boiling point passing over at 225°/15 mm., but this contains too little bromine, and can be proved to contain considerable quantities of the di-lactone ester melting at 140° (q.v.), formed by the elimination of ethyl bromide during the process of distillation. As a matter of fact, the separation of the di-lactone ester and the unchanged dibromo-ester in this mixture can be easily effected by the aid of cold benzene, in which the former is insoluble. The crude dibromo-ester is therefore not distilled prior to analysis, but purified as far as possible by placing it in an exhausted desiccator over potassium hydroxide for several days:

0·3429 gave 0·2853 AgBr. Br = 35·41.
$C_{14}H_{22}O_6Br_2$ requires Br = 35·9 per cent.

The Di-lactone of ββ-Dihydroxydimethylpropanecarbethoxydicarboxylic Acid (XVI, p. 599).

This substance can be prepared, as mentioned above, by distilling the dibromo-ester under diminished pressure, but is best obtained in quantity by boiling 60 grams of the ester mixed with 100 grams of pyridine for six hours on the sand-bath. The product is isolated by pouring it into dilute hydrochloric acid, extracting the oil with ether, and washing the ethereal extract with dilute hydrochloric acid. The residue which is left after evaporating the ether from the dried solution is an oil, which distils at 230°/20 mm. and solidifies in the receiver.

It crystallises from benzene in small, flattened needles, and from hot water in glistening plates melting at 140°:

0·1705 gave 0·3322 CO_2 and 0·0812 H_2O. C = 53·11; H = 5·29.
$C_{10}H_{12}O_6$ requires C = 52·6; H = 5·3 per cent.

The compound dissolves in cold aqueous alkalis.

The Di-lactone of ββ-*Dihydroxydimethylpropanetricarboxylic Acid* (XVII, p. 599).

The di-lactonic ester is readily hydrolysed when it is boiled with dilute hydrochloric acid (16 per cent. aqueous solution) for four hours, and the corresponding acid separates from the solution when it is evaporated to a small bulk. It crystallises from ethyl acetate in glistening needles, which melt at 186°:

0·1269 gave 0·2230 CO_2 and 0·0470 H_2O. C=47·92; H=4·10.

$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The compound is not readily soluble in cold water, but quickly dissolves on warming; it does not, however, separate from its hot concentrated aqueous solutions on cooling, and it is evident that some transformation into the hydroxy-acid takes place under these conditions. The well-defined needles fall to a fine powder, without loss of weight, when they are heated for a long time at 100°, and it is probable, therefore, that at this temperature some change in crystalline form occurs.

The *silver* salt, obtained from the neutral ammonium salt, is a white, micro-crystalline precipitate, which is evidently the salt of *the dihydroxy-tribasic acid*:

0·2783 gave 0·1615 Ag. Ag=58·03.

$C_8H_9O_8Ag_3$ requires Ag=58·2 per cent.

The Three Stereoisomeric Forms of Carboxymethane-$II^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylic Acid* (XVIII, p. 599).

It has already been shown (T., 1915, **107**, 1096) that the action of concentrated aqueous alkali hydroxide at a high temperature leads to the formation of carbon to carbon rings, even in those compounds in which the γ-position of the bromine atoms would, under normal conditions, cause them to pass into the corresponding lactones. The formation of the above acids instead of the lactone already described furnishes another example of the efficacy of this process. Actually, under the conditions described below, no trace of the di-lactonic acid could be found in the product. Sixty grams of potassium hydroxide are dissolved in 50 c.c. of water, and the solution is evaporated over the free flame until it reaches a temperature of 150°. Fifteen grams of the dibromo-ester mixed with an equal volume of alcohol are now added as quickly as possible, consistent with safety, and the very vigorous reactiou is allowed to subside. It is well to use a large flask for this operation, as the reaction is almost explosive in its violence,

and some of the material is apt to be lost by spurting. The three acids separate together when the concentrated aqueous solution is acidified with hydrochloric acid, and can be isolated in the following manner. The well-dried mixture is ground with an equal volume of clean, white sand and heated at 160°, with frequent stirring, for six hours. The cooled product is then ground, transferred to a Soxhlet apparatus, and extracted with carefully dried and purified ether. The ethereal extract, on evaporation, leaves a solid residue, which yields the meso-cis-*acid* (formula [*a*], p. 599), in slender needles, when it is boiled with a little water and the solution, mixed with an equal volume of concentrated hydrochloric acid, is allowed to cool. This acid melts at 154° and evolves steam at a few degrees above this temperature:

0·1394 gave 0·2451 CO_2 and 0·0518 H_2O. C=47·96; H=4·13.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The acid is insoluble in dry ether or benzene. It can be recrystallised from concentrated aqueous solutions, but is best purified by recrystallisation from hydrochloric acid.

The *silver* salt, prepared in the usual manner, is a white, apparently amorphous, precipitate:

0·3142 gave 0·1952 Ag. Ag=62·12.
$C_8H_5O_6Ag_3$ requires Ag=62·2 per cent.

The Anhydro-acid (XIX, p. 599, configuration [*a*]).—The acid reacts readily with acetyl chloride at the temperature of the boiling reagent, and the above substance remains as a white, crystalline solid when the chloride is evaporated. It crystallises from benzene containing a little light petroleum (b. p. 60—80°) in small plates, which melt at 103°:

0·1771 gave 0·3418 CO_2 and 0·0543 H_2O. C=52·64; H=3·41.
$C_8H_6O_5$ requires C=52·7; H=3·3 per cent.

The anhydro-acid when boiled with water yields the acid from which it was derived.

The *racemic acid* (formula [*c*], p. 599) can be isolated in a similar manner from the sand remaining in the Soxhlet apparatus, and for this purpose the sand is transferred to a glass Carius tube, mixed with a sufficient quantity of acetic anhydride, and the sealed tube heated at 220° for six hours. The product is then freed from acetic anhydride by evaporation, the residue ground, and again extracted with dry ether in a Soxhlet apparatus. In this case, it is best to purify the product left after evaporating the ether by recrystallisation from benzene, from which solvent it is obtained in lustrous plates melting at 121°. The following analysis

shows it is be the *anhydro-acid* of the racemic acid (XIX, p. 599, configuration [*c*], p. 599):

0·1737 gave 0·3344 CO_2 and 0·0531 H_2O. C=52·50; H=3·40.
$C_8H_6O_5$ requires C=52·7; H=3·3 per cent.

The anhydro-acid readily passes into solution when warmed with water, and the addition of an equal volume of concentrated hydrochloric acid precipitates the *racemic acid* in small prisms, which melt at 165°, the fused acid remaining unaltered at 300°:

0·1305 gave 0·2294 CO_2 and 0·0484 H_2O. C=47·95; H=4·12.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The acid is insoluble in dry ether or benzene. It is characterised by giving an insoluble calcium salt, which is precipitated when a neutral solution of the ammonium salt is boiled with calcium chloride solution.

The *silver* salt is similar in appearance to that of the *meso-cis*-acid:

0·2987 gave 0·1856 Ag. Ag=62·13.
$C_8H_5O_6Ag_3$ requires Ag=62·2 per cent.

The meso-trans-*acid* (formula [*b*], p. 599) can be obtained from the sandy residue on extraction with hot water, and separates when concentrated hydrochloric acid is added to the solution previously concentrated by evaporation. It is appreciably less readily soluble in water than either the *meso-cis-* or the racemic acid, and can be recrystallised from this solvent. It is, however, advisable to use dilute hydrochloric acid for this purpose, when the acid is obtained as a crystalline powder which melts at 193°:

0·1407 gave 0·2468 CO_2 and 0·0521 H_2O. C=47·73; H=4·11.
$C_8H_8O_6$ requires C=48·0; H=4·0 per cent.

The acid does not react with acetic anhydride at a high temperature, and does not appear to possess any tendency towards anhydride formation. It can, as a matter of fact, be distilled in small quantities without undergoing any change. It is insoluble in dry ether and in benzene.

The *silver* salt is a white, sandy powder:

0·2489 gave 0·1544 Ag. Ag=62·03.
$C_8H_5O_6Ag_3$ requires Ag=62·2 per cent.

The acid forms a characteristic *calcium* salt similar in appearance to that of the racemic acid, but differing from it in being precipitated when the solution containing the neutral ammonium salt and calcium chloride is boiled, and redissolving when it is cooled.

Attempts to Convert the Three Stereoisomeric Acids into one another, leading to Fission of the Ring Systems.

All three acids remain unaltered after prolonged boiling with aqueous hydrochloric acid, and can also be recovered unchanged after having been heated in a sealed tube, in 20 per cent. aqueous solution, for six hours at 200°. When, however, 3 grams of either acid are mixed with 30 c.c. of concentrated hydrochloric or hydrobromic acid and the solution is heated in a sealed tube at 220° for ten hours, no trace of unchanged acid can be found in the product. In its place there is formed an insoluble, crystalline substance, which, after recrystallisation from ethyl acetate, is obtained in glistening needles melting at 186°. This compound is without doubt the di-lactonic acid of formula XVII (p. 599), a fact which can be shown by direct comparison and also by the following analyses:

Found: C = 47·85; H = 4·07.

$C_8H_8O_6$ requires C = 48·0; H = 4·0 per cent.

Found: Ag = 58·12.

$C_8H_9O_8Ag_3$ requires Ag = 58·2 per cent.

Bromination of the Three Stereoisomeric Acids.

The meso-cis-*Acid*, m. p. 154° (formula [*a*], p. 599).—The bromination of this acid proceeds very smoothly when 10 grams of the acid are treated with 64 grams of phosphorus pentabromide and 8·5 grams of bromine, the operation being carried out in the usual way at the ordinary temperature, and being finished by warming on the water-bath. The product, when poured into well-cooled alcohol, yields an oil on dilution with water, which can be extracted with ether. The washed and dried extract leaves cis-*ethyl bromocarbethoxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylate* (XXI, p. 601) on evaporating the solvent. The bromo-ester distils without decomposition at 207°/12 mm., and is a clear, fairly mobile oil:

0·1813 gave 0·0930 AgBr. Br = 21·83.

$C_{14}H_{19}O_6Br$ requires Br = 22·0 per cent.

The bromo-ester is recovered unchanged even after prolonged boiling with pyridine, but when hydrolysed by boiling with an alcoholic solution containing one and a-half times the calculated quantity of potassium hydroxide, it is hydrolysed to cis-*bromocarboxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylic acid* (XXII, p. 601), which can be isolated by evaporating the solution

free from alcohol, acidifying, and filtering. This acid crystallises from hot water in small needles, which melt at 171°:

0·2203 gave 0·1473 AgBr. Br = 28·45.

$C_8H_7O_6Br$ requires Br = 28·6 per cent.

The *bromo-anhydro-acid* (XXIII, p. 601) is readily obtained from the above bromo-acid by boiling it for an hour on the water-bath with excess of acetyl chloride, and is left as a crystalline residue when the reagent is evaporated. It crystallises from benzene in colourless plates, which melt at 139°:

0·1910 gave 0·1373 AgBr. Br = 30·59.

$C_8H_5O_5Br$ requires Br = 30·7 per cent.

The anhydro-acid when boiled with water yields the acid from which it was derived. It should be added that in all the three compounds described above, the halogen is very strongly combined, and is, in fact, almost aromatic in character. For example, the usual test by boiling with fuming nitric acid and silver nitrate in a test-tube fails to reveal the presence of bromine in them.

The Racemic Acid, m. p. 165° (formula [*c*], p. 599).—This acid is brominated in precisely the same way as the *meso-cis*-acid, and it gives r-*ethyl bromocarbethoxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1:2-*dicarboxylate* (XXIV, p. 602) with equal readiness. The ester undergoes partial decomposition on distillation under diminished pressure, and it is therefore best to use the crude product, which can be sufficiently purified by placing it in an exhausted desiccator over potassium hydroxide for some days:

0·1994 gave 0·1018 AgBr. Br = 21·71.

$C_{14}H_{19}O_6Br$ requires Br = 22·0 per cent.

The bromo-ester reacts quickly when it is boiled with three times its volume of pyridine for three hours, and the product can be isolated by pouring the mixture into excess of dilute hydrochloric acid and extracting with ether. The dried ethereal extract leaves a solid residue on evaporation, which is the *lactone* of *hydroxycarbethoxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1-*carbethoxy-2-carboxylic acid* (XXV, p. 602), a substance which crystallises from benzene in small needles melting at 87°:

0·1365 gave 0·2832 CO_2 and 0·0689 H_2O. C = 56·59; H = 5·61.

$C_{12}H_{14}O_6$ requires C = 56·7; H = 5·5 per cent.

The lactonic ester dissolves in cold aqueous alkalis, and, if a sufficient quantity of the reagent is used, it is hydrolysed at the boiling point in the course of an hour. The solution, after being freed from alcohol by evaporation, is acidified, when the *lactone* of *hydroxycarboxymethane*-II$^{1:3}$-3-*methyl*cyclo*propane*-1 : 2-*dicarb-*

oxylic acid (XXVI, p. 602) is precipitated. The compound crystallises from benzene in groups of needles and melts at 137°:

0·1420 gave 0·2519 CO_2 and 0·0398 H_2O. C = 48·38; H = 3·12.
$C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.

The *silver* salt, prepared from a neutral solution of the ammonium salt, is evidently that of the tribasic hydroxy-acid:

0·2417 gave 0·1454 Ag. Ag = 60·15.
$C_8H_5O_7Ag_3$ requires Ag = 60·3 per cent.

The lactonic acid does not separate well either from water or from dilute hydrochloric acid. The corresponding hydroxy-acid could not be isolated.

The meso-trans-*Acid*, m. p. 193° (formula [*b*], p. 599).—The method of bromination is the same as that given in the case of the *meso-cis*-acid, and the operation proceeds with the same readiness. When, however, the product is poured into alcohol, it will be found that the oil which is subsequently precipitated by the addition of water is free from bromine. When collected in the usual way and fractionated under diminished pressure, it yields *ethyl methylmethane*-III$^{1:2:3}$-cyclo*propane*-1 : 2 : 3-*tricarboxylate* (XXVII, p. 602) as a colourless, fairly mobile oil boiling at 183°/12 mm.:

0·1501 gave 0·3268 CO_2 and 0·0879 H_2O. C = 59·37; H = 6·51.
$C_{14}H_{18}O_6$ requires C = 59·6; H = 6·4 per cent.

Methylmethane-III$^{1:2:3}$-cyclo*propane*-1 : 2 : 3-*tricarboxylic Acid* (XXVIII, p. 602).

The hydrolysis of the tribasic ester is effected by boiling it with an alcoholic solution containing 1·5 times the theoretical quantity of potassium hydroxide for two hours, and is obtained by acidifying the solution after it has been freed from alcohol by evaporation. The acid is purified by recrystallisation from dilute hydrochloric acid. It forms small, well-defined prisms, which melt at 149°:

0·1702 gave 0·3020 CO_2 and 0·0475 H_2O. C = 48·40; H = 3·10.
$C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.

The *silver* salt, prepared from the neutral ammonium salt, is a white, micro-crystalline precipitate:

0·2003 gave 0·1247 Ag. Ag = 62·25.
$C_8H_3O_6Ag_3$ requires Ag = 62·4 per cent.

The acid is freely soluble in warm water, but is insoluble in ether or benzene. It is not acted on by acetic anhydride at a

high temperature, and can be distilled in small quantities at the ordinary pressure without undergoing change. There is, apparently, no tendency whatever for it to pass into an anhydro-acid. It is stable towards bromine, even when heated, and does not decolorise alkaline permanganate in the cold, although it is slowly attacked by the boiling reagent, and, from the products, methylsuccinic acid, melting at 112°, can be isolated (Found: C = 45·28; H = 6·18. $C_5H_8O_4$ requires C = 45·4; H = 6·1 per cent.). It is not affected by prolonged boiling with aqueous acids or alkalis. An attempt was made to convert the acid into an isomeride by heating it in a sealed tube with concentrated hydrochloric acid for ten hours at 220°, and under these conditions it is converted into another substauce, which separates in a crystalline condition when the contents of the tube are cooled. This compound is not, however, a stereoisomeride, but is the *tri-lactone* of *α-hydroxy-ββ-dihydroxydimethylpropanetricarboxylic acid* (XXX, p. 602), which can be recrystallised from a large quantity of benzene and obtained in ill-defined crystals melting at 206°:

0·1667 gave 0·2957 CO_2 and 0·0467 H_2O. C = 48·39; H = 3·11.
$C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.

The *silver* salt, prepared from the neutral ammonium salt, is a white, amorphous precipitate, and is evidently the salt of the trihydroxy-tribasic acid:

0·2179 gave 0·1230 Ag. Ag = 56·44.
$C_8H_9O_9Ag_3$ requires Ag = 56·5 per cent.

The lactone is soluble in warm water, but does not crystallise well on cooling, although the separation is facilitated by the addition of an equal volume of concentrated hydrochloric acid to the concentrated aqueous solution. It is probable that solution in water converts some of the lactone into the hydroxy-acid, although all attempts to prepare this acid were unsuccessful.

(2) *The Tribromination of ββ-Dimethylpropanetricarboxylic Acid.*

The method is the same as that described in the case of dibromination, only 120 grams of bromine are used in place of 80 grams. The final atom of bromine is absorbed with considerable difficulty, and it is advantageous, after adding sufficient bromine to form the dibromo-compound, to add the remaining molecule at once, and to leave the mixture at 60° for twenty-four hours before final completion on the water-bath. Care must, of course, be taken to exclude moisture throughout this operation by the provision of a calcium chloride tube at the end of the con-

denser. It will be found, moreover, that the rate of absorption is increased if a trace of iodine is added.

The product is then poured into well-cooled alcohol, and the oil precipitated by water in the usual manner, the ethereal extract being washed with water and then with sodium carbonate solution. The residue left after the evaporation of the dried ethereal solution contains too little bromine (Found: Br = 36·31. $C_{14}H_{21}O_6Br_3$ requires Br = 45·7 per cent.), and it is, therefore, in all probability mixed with either the di- or the tri-lactone. That this is actually the case can be shown by mixing the oil with an equal volume of benzene, when a crystalline solid slowly separates. The filtrate deposits more of this solid on keeping, and this, after collection, leaves a filtrate which, when freed from the solvent, consists of *ethyl α-bromo-ββ-dibromodimethylpropanetricarboxylate* (XXIX, p. 602) in an approximately pure condition:

0·2101 gave 0·2190 AgBr. Br = 44·36.

$C_{14}H_{21}O_6Br_3$ *requires* Br = 45·7 *per cent.*

Unfortunately, the bromo-ester cannot be distilled without undergoing decomposition, and the above product is the purest form of the compound we were able to prepare.

The solid material obtained in the above purification yields a small quantity of the tri-lactone, melting at 206°, when repeatedly recrystallised from benzene, but it also contained other compounds, which we were not able to isolate in a pure condition.

Action of Pyridine.—When the tribromo-ester is boiled with three times its volume of pyridine and the product is poured into dilute hydrochloric acid, a crystalline substance slowly separates, which is shown to be the *tri-lactone* of *α-hydroxy-ββ-dihydroxydimethylpropanetricarboxylic acid* (XXX, p. 602), melting at 206°, by direct comparison and by the following analysis:

Found: C = 48·31; H = 3·06.

$C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.

Action of Concentrated Aqueous Potassium Hydroxide.—The operation is the same as that described in the case of the dibromo-ester (p. 610). The product, when acidified, yields a crystalline precipitate, from which, by repeated recrystallisation from dilute hydrochloric acid, a small quantity of *methylmethane*-III$^{1:2:3}$-cyclo*propane*-1:2:3-*tricarboxylic acid* (XXVIII, p. 602), melting at 149°, can be isolated (Found: C = 48·38; H = 3·12. $C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.), the yield being only 12 per cent. of that theoretically possible. The remainder of the product of this reaction is undoubtedly the tri-lactone (XXX, p. 602),

as this substance can be isolated in considerable quantities from the acid mother liquors.

Many of the experiments described in this paper were carried out at the University of Sheffield by Mr. A. S. Wood, to whom our thanks are due.

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LXV.—*Colouring Matters of Red and Blue Fluorite.*

By CECIL STEVENSON GARNETT.

IN a recent paper, Blount and Sequeira (T., 1919, **115**, 705) showed that a minute amount of organic matter could be extracted from "Blue John" by means of various solvents, and draw the conclusion that the colonr of the mineral is of organic origin

The experiments now to be described appear to confirm the above conclusion, but also carry the investigation somewhat further.

A quantity of extremely deep blue fluorite was discovered by the author near the famous "Blue John Mine" some years ago; the colour was uniform, and so deep that at a short distance a small lump appeared almost as black as coal. On very thin slices being cut from this material, however, it was seen to be of a beautiful deep blue, its apparent blackness being due to extreme depth of colour. Spar of this character is not sent from the mine from which the previous authors obtained their specimens.

A sample was finely powdered and extracted successively with chloroform, benzene, and ether, and although there was no apparent diminution in colour, it would be difficult to say that this was not the case, as in fine powder even so dark a specimen had such a pale blue colour that a slight further diminution in tint would scarcely be perceptible. The carbon content determined by combustion was 0·27 per cent. before, and 0·207 per cent. after, extraction. Similar determinations on other samples showed a decrease in carbon content with a decrease in colour. The amount of carbon found in the very dark specimen is nearly five times the

amount contained in the specimen quoted by Blount and Sequeira (0·046 per cent.).

The powdered mineral, when heated with concentrated sulphuric acid, yielded a black, carbonaceous residue, but when heated with a mixture of sulphuric and nitric acids, the blue compound was readily oxidised, leaving a colourless residue of fluorite (and, of course, calcium sulphate). When heated alone, a very pronounced bituminous odour was observed, and a residue of clear, colourless fluorite remained; the odour was quite different from the resinous one produced by heating specimens of "Blue John" which have been polished and made into fancy goods.

Distillation of "Blue John."

The actual separation of bituminous matter was next attempted. A hard-glass tube was almost filled with the powdered, extracted fluorite, and a small U-tube (merely air-cooled) attached. On heating, a yellowish-brown oil collected in the cool parts of the apparatus, and an inflammable gas issued from the jet. The gas burned steadily and freely until the distillation had proceeded to completion, when a residue of colourless fluorite remained. The inside of the glass tube had, however, gained a mirror-like coating of carbon, evidently resulting from the decomposition of the vapour after being driven from the fluorite and on coming in contact with the red-hot walls of the tube.

The removal of the colouring matter without the deposition of carbon within the tube was now attempted, and was easily accomplished by immersing the tube containing the powdered fluorite in a bath of molten tin. Oil again collected, but much less inflammable gas was obtained, and no deposition of carbon occurred on the walls of the tube. The removal of the colouring matter was, in these experiments, evidently accomplished only by its destructive distillation.

In order to ascertain the distribution of the colouring matter within the fluorite, thin sections were examined microscopically. It was observed that the colouring matter is not homogeneously distributed in a fine state of division within the fluorite crystals, but that it occurs as films therein. The depth of colour depends on the abundance and thickness of the films existing in the fluorite, which is itself clear and colourless. They occur parallel to and in the plane of the faces of the crystal (cube), and also at the crystalline junctions, in such a manner as to point to the conclusion that the colouring matter was deposited as films on the surfaces of the crystals at intervals during their growth. The banded coloration

of "Blue John" is explained by this supposition. The blue colour imparted by the bituminous matter is probably due to the chemical combination in which the latter exists.

Red Fluorite.

Mawe ("Mineralogy of Derbyshire," 1802) states that ruby-coloured fluorite in perfect cubes is said to have been found in Derbyshire. No other occurrence of this rare variety of fluorite in Derbyshire appears to have been observed until the present author recorded having found a quantity of it near Ashover. The colour of this specimen is not pink, as are the specimens usually seen in museums, but definitely red.

The colour of this variety is not due to organic matter, and the appearance is scarcely altered by prolonged exposure to a bright red heat. The colouring matter is readily and completely extracted from the roughly crushed fluorite by boiling hydrochloric or nitric acids, leaving a residue of clear, colourless fluorite. The solution was fonnd to contain rare earths and nothing but insignificant traces of any other element. The oxalates and sulphates were obtained as usual, and an attempt was made to separate and identify the rare earth elements present, but was not continued, on account of the well-known difficulties which such a task presents.

Microscopical examination of thin sections showed that the colouriug matter is distributed as films in colourless fluorite. Instead, however, of the films occurring chiefly within the crystal (as in the case of "Blue John"), they appear to exist chiefly (at least) at the crystalline junctions within the mass (as in the case of fluorite coloured brown by limonite). The redness of the colour is due to the thinness of the films, as the mineral of which they consist may be occasionally found in tiny cavities in the fluorite; it is massive, black, opaque, and pitch-like in appearance. Microscopical examination of films of varying thickness (as they occur) confirms the chemical evidence as to the identity of the black, "rare earth" mineral and the films.

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LXVI.—*Studies in Catalysis. Part XIII. Contact Potentials and Dielectric Capacities of Metals, in Relation to the Occlusion of Hydrogen, and Hydrogenation.*

By William Cudmore McCullagh Lewis.

In two earlier papers in this series (T., 1919, **115**, 182, 1360), heterogeneous catalysis was considered from the point of view of the critical increment and the radiation hypothesis of chemical reactivity. It was pointed out that the essential function of such a catalyst was to reduce greatly the critical increment of activation of one or more of the reactants, thereby increasing the rate of the reaction. The effect was considered as induced at the surface of the catalyst on which at least one of the reactants was adsorbed. The same idea is obviously applicable to any case in which one or more of the reactants is capable of being actually dissolved by the catalyst and emitted from its surface in the activated form. Snch a case is encountered in the activation of hydrogen as a result of occlusion by certain metals.

The Critical Increment, E_{H_2} of Dissociation of Hydrogen into Atoms when dissolved in a Metal.

In an extended series of papers, Sieverts has measured the solubility of hydrogen in various metals over a wide range of temperature. He has found that, in general, the concentration of the dissolved gas varies as the square root of the pressure of hydrogen in the gas phase, indicating that the hydrogen is dissociated into atoms or ions. The most trustworthy results are those obtained with nickel, iron, and copper (*Zeitsch. physikal. Chem.*, 1911, **77**, 591), in which it was found that the solubility of hydrogen is higher in nickel than in iron, and greater in iron than in copper. Sieverts has shown that the process is one of true solubility, and not simply surface adsorption, although the latter is necessarily present as well.

The solubility of hydrogen in these and in other metals increases markedly as the temperature rises. Applying the well-known thermodynamic relation to the variation of the solubility, S, with the temperature, we have

$$d \log S/dT = Q/RT^2,$$

where Q stands for the heat absorbed in the process at constant volume. Postulating that the process is

$$H_2 \longrightarrow 2H,$$

and assuming, as has been done in another connexion, that the critical increment of union of the free atoms is zero, it follows that Q is identical with E_{H_2}, the critical increment of dissociation per gram-molecule of hydrogen in the dissolved state. From Sieverts' values of the solubility of hydrogen, it is thus possible to calculate E_{H_2} at various temperatures. The following results have thus been obtained. The solubility, S, is expressed in milligrams of gas per 100 grams of metal.

Nickel.

t.	S.	$d \log S/dT$.	E_{H_2} in cals.
315°	0·22	$3{\cdot}05 \times 10^{-3}$	2099
822	0·72	$1{\cdot}66 \times 10^{-3}$	3984
1225	1·333	$1{\cdot}30 \times 10^{-3}$	5824

In the neighbourhood of 150°, E_{H_2} is calculated to be approximately 1700 cals. It will be observed that as the temperature rises the value of E_{H_2} also increases. This is discussed later.

Iron.

t.	S.	$d \log S/dT$.	E_{H_2}.
514°	0·075	$5{\cdot}3 \times 10^{-3}$	6560
775	0·201	$3{\cdot}0 \times 10^{-3}$	6590

In the neighbourhood of 150°, E_{H_2} is estimated to be 6500 cals.

Copper.

t.	S.	$d \log S/dT$.	E_{H_2}.
620°	0·030	$5{\cdot}0 \times 10^{-3}$	7975
827	0·072	$4{\cdot}2 \times 10^{-3}$	9080
904	0·102	$4{\cdot}0 \times 10^{-3}$	11080
981	0·132	$3{\cdot}8 \times 10^{-3}$	11930

In the neighbourhood of 150°, E_{H_2} is of the order of 5000 cals. It is impossible to extrapolate with accuracy, as the experimental results at the lowest temperatures are evidently somewhat discordant.

Platinum (Sieverts, *Ber.*, 1912, **45**, 221).

t.	S.	$d \log S/dT$.	E_{H_2}.
1136°	0·036	$4{\cdot}4 \times 10^{-3}$	17480
1239	0·055	$4{\cdot}2 \times 10^{-3}$	19200

Actual extrapolation to low temperatures is impossible in this case. It is evident, however, that E_{H_2} in the neighbourhood of 150° lies between 10,000 and 15,000 cals.

In general, the lower the solubility the greater is the critical increment. A large critical increment means that the metal in question has a relatively small dissociating power.

It must be emphasised that the values in the last table refer to absorption by metallic platinum. If hydrogenation is due to atomic hydrogen which has been brought into existence by the act of dissolving, it follows that metallic platinum is a less efficient catalyst than copper. In the case of platinum-black, however, Mond, Ramsay, and Shields (*Phil. Trans.*, 1896, [*A*], **186**, 657) have shown that the quantity of hydrogen absorbed is very much greater than it is in massive platinum, and, further, that the quantity absorbed diminishes as the temperature rises. In the case of platinum-black, we are probably dealing with adsorption alone.

Sieverts has shown that hydrogen is soluble in cobalt, the solubility becoming measurable above 700°. The same author has also found that hydrogen is insoluble in pure silver. Similarly, in the case of gold, the solubility is too low to be measured. Hydrogen is likewise insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, and aluminium (compare *Zeitsch. Elektrochem.*, 1910, **16**, 708). Aluminium, however, forms a hydride above 800°. One would expect those metals in which hydrogen is insoluble to be negative catalysts for hydrogenation if they partly or wholly cover the surface of the catalytically active metal.

On the view advanced in the present paper, the conclusion is that the insolubility of hydrogen in the metals mentioned is due to the inability of these metals to dissociate the gas.

The solubility of hydrogen in tungsten is extremely low (Sieverts, *Ber.*, 1911, **44**, 2394). On the other hand, the solubility of hydrogen in tantalum is very high, and diminishes as the temperature rises, although proportional to the square root of the hydrogen pressure. The case is analogous to that exhibited by palladium over a certain temperature range, a compound being formed which dissociates with absorption of heat.

The Variation of E_{H_2} with Temperature, and the Dielectric Capacity of the Metal.

As the foregoing calculations show, the apparent critical increment of dissociation of molecular hydrogen rises steadily as the temperature increases. The simplest explanation of this is to

assume that the dissociating power of the metal diminishes as the temperature rises, this being the usual effect of temperature on this property. From the point of view of electrostatic attractions between the constituent parts of a dissolved molecule, we should expect, in accordance with the Thomson-Nernst rule, that the value of E_{H_2} would vary inversely as the dielectric capacity of the metal or inversely as the square of the refractive index of the wave-length corresponding with the value of E. To dissociate molecular hydrogen in the gaseous state into atoms requires an absorption of 85,000 cals. per gram-molecule. If atomic hydrogen is formed in metals, it would follow that the dielectric capacity, D_0, of nickel, for example, in the region of 150° is given by the relation

$$1700 = 85000/D_0,$$

whence $D_{Ni} = 50.$

Similarly, $D_{Fe} = 13, \; D_{Cu} = 17,$

and $D_{Pt} = 6 \text{ to } 8.$

On the classical electromagnetic theory, the dielectric capacities of metals were regarded as infinite. This conclusion has been shown not to be necessary by Sanford (*Physical Rev.*, 1918, [ii], **12**, 130), who concludes from experiments on contact electrification that metals possess dielectric capacities of the same order of magnitude as those of non-metals. In Sanford's experiments, no precautions appear to have been taken to remove surface films (adsorbed moisture and gases), so that the estimated magnitude of D is probably incorrect.

If it could be shown that a true Volta potential difference exists between two pure metals in contact, this would point to the reality of finite dielectric capacities. The problem of the existence of such potential differences has been under discussion since the time of Volta himself. Within recent years, however, the evidence obtained from the study of thermionic currents and photo-electric effects has lent very strong support to the original view of Volta. This evidence is discussed in detail by Langmuir (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 129), who has shown that several independent methods lead to substantially the same values for the contact potential. Langmuir's conclusions regarding the real existence of such potential differences appears to be incontrovertible.

Calculation of the Contact Potential Difference on the Basis of a Finite Dielectric Capacity attributed to a Metal.

As shown by Langmuir, the contact potential difference which comes into existence when two metals are brought into intimate

contact can be regarded as the difference of two "imaginary" potential differences, each of which is characteristic of a given metal. This potential difference, which may be called conveniently the *characteristic potential* of a metal, and is denoted by the symbol Φ is a measure of the forces which hold an electron in the metal and prevent its escape. It is "imaginary" in the sense that it does not come into existence until the electron is in the act of leaving the surface. The values of Φ for a number of metals have been obtained from observations on thermionics, the threshold frequency of the normal photo-electric effect, and line-spectra resonance measurements, the results being concordant.

If we assume the existence of a finite dielectric capacity as characterising a metal, it should be possible to calculate the work done in removing an electron from the metal to free space, thereby obtaining a value of Φ which may be compared with the mean value given by Langmuir. Let us denote by W the work required to extract an electron and bring it into free space, theoretically at infinite distance from the metal surface. Employing the inverse square law, which is known to hold down to distances of the order of atomic dimensions, although not down to nuclear and electronic dimensions, we obtain

$$W = e^2 \int_{r_0}^{\infty} \frac{dr}{Dr^2}$$

where D is the dielectric capacity at any position r. The dielectric capacity alters continuously as we pass from the metal to free space, its value being D_0 in the metal and unity in free space. The simplest mode of allowing for this variation is to write

$$D = D_0^{r_0/r}$$

where r_0 is the average distance apart of an electron and a metallic ion in the metal. Lindemann (*Phil. Mag.*, 1915, [vi], **29**, 127) has put forward a number of considerations for regarding the metallic state as being composed of two interwoven space lattices, one an electron lattice, the other an ionic one. On the average, an electron will be separated from an ion by a distance r_0, which is one half the distance between two contiguous ions. Langmuir (*loc. cit.*) has pointed out that in the case of the simple face-centred cubic lattice, which is characteristic of copper and silver, the shortest distance, σ, between two adjacent atoms is given by

$$\sigma = 1{\cdot}33 \times 10^{-8} . V^{1/3}$$

where V is the atomic volume. From the values of σ thus calculated by Langmuir, we can obtain the value of r_0.

On integrating the expression for W, we obtain

$$W = \frac{e^2}{r_0 \log_e D_0}\left(1 - \frac{1}{D_0}\right).$$

This must be equivalent to Φe, whence

$$\Phi = \frac{e}{r_0 \log_e D_0}\left(1 - \frac{1}{D_0}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We have now to evaluate this expression for certain metals, using the approximate values of D_0 which we have obtained for the temperature 150°.

Copper.—$D_0 = 17$. $\sigma = 2{\cdot}56 \times 10^{-8}$ cm. Hence $r_0 = 1{\cdot}28 \times 10^{-8}$. 1 E.S.U. $= 3 \times 10^2$ volts. Hence $\Phi = 3{\cdot}8$ volts.

The weighted mean value obtained by Langmuir from the results of various observers is $\Phi = 4{\cdot}0$ volts.

Iron.—$D_0 = 13$. $= 2{\cdot}56 \times 10^{-8}$ cm. Hence $r_0 = 1{\cdot}28 \times 10^{-8}$. Hence $\Phi = 3{\cdot}5$ volts.

Langmuir's value is 3·7 volts.

Platinum.—$D_0 = 7$ approximately, whence $\Phi = 4{\cdot}97$ volts. Langmuir gives the value 4·4 volts with a query. Values greater than 5 volts have been obtained by various observers.

In general, the agreement between the accepted value of Φ and that calculated by means of equation (1) is satisfactory. To this extent we are justified, therefore, in attributing a finite dielectric capacity to a metal.

Nickel.—$D_0 = 50$. Taking r_0 to be the same as that for copper, we find that $\Phi = 2{\cdot}8$ volts. The characteristic potential for nickel has not as yet been determined by any direct method. It follows from the above value that if copper and nickel are brought into contact, the nickel should be positive with respect to the copper, the contact potential difference being $3{\cdot}8 - 2{\cdot}8 = 1$ volt.

From the observed values of Φ quoted by Langmuir, we can calculate the dielectric capacity of the corresponding metal by means of equation (1). We thus find the following values in a few typical cases:

Metal.	Φ in volts.	$r_0 \times 10^8$.	D_0.
Silver	4·1	1·45	8
Zinc	3·4	1·40	18
Aluminium	3·0	1·45	30
Lithium	2·35	1·57	40
Sodium	1·82	1·91	60

It is evident from the above values that the dielectric capacity does not completely determiue the solubility of hydrogen in a metal. Thus, metals such as zinc, bismuth, and tin possess higher dielectric capacities than platinum, yet hydrogen is soluble in

platinum and insoluble in these metals. It is noteworthy that the alkali metals, which apparently possess very high dielectric capacities, are capable of forming hydrides. Aluminium, which also has a fairly high capacity, forms a hydride at higher temperatures. This cannot be a general rule, however, for nickel does not apparently form a hydride. We must seek, therefore, some other factor as an equally significant quantity.

The capability of a metal of dissolving hydrogen, and, in the limit of forming a hydride, depends, not only on the dielectric capacity, but also on the type of radiant energy which the metal is able to supply to dissociate the gas when the latter has entered the surface. In virtue of the temperature of the metal, all types (frequencies) of radiation are present, although to very different extents. The metal is capable of enhancing the density of certain types, thereby increasing the dissociating effect provided the frequencies are sufficiently high.

Source of the Energy which Dissociates Hydrogen in a Metal.

The atoms of a metal possess energy in respect of vibration and also in respect of rotation (Honda, *Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, No. 2), the latter being a negligible quantity so far as specific heats are concerned, until high temperatures are reached. Honda considers that the act of fusion, and the latent heat connected therewith, depend on this energy of rotation. If an atom possessing the amount of energy corresponding with its latent heat of fusion is brought to rest, this energy will be emitted. The author suggests that this is the source of the energy which brings about dissociation of the hydrogen in the metal. In this connexion, it is noteworthy that the metals which are capable of dissociating hydrogen are those with the highest values for the latent heat of fusion. The following table contains some of the values quoted by Honda:

Metal.	Latent heat of fusion per gram-atom L.	D_0.	$D_0 \times L$
Pt	5360	Ca 7	37,520
Pd	3860	—	—
Fe	3348	13	43,524
Ni	2710	50	135,500
Cu	2650	17	45,050
Ag	2270	8	18,160
Al	2160	30	64,800
Zn	1840	18	33,120
Cd	1540	—	—
Pb	1118	—	—
Na	730	60	43,800
Hg	562	—	—

If all metals possessed the same dielectric capacity, the valu(the latent heat of fusion should distinguish those metals wh dissolve hydrogen from those which do not. The dielectric capa(varies, however, from metal to metal, with the result that e sodium is capable of forming a hydride, and therefore of (solving or dissociating the gas. The dissociating power depe simultaneously on the dielectric capacity and the density of t suitable energy. If the dielectric capacity is small, the ene required is correspondingly great, and the available energy of t type considered may be insufficient, especially as the higher t latent heat of fusion the fewer are the number of atoms at a giv temperature which possess the corresponding energy. Th tungsten appears to have the highest characteristic potential (any element so far investigated. This means that tungsten has very low dielectric capacity, and, consequently, the energy require to dissociate and dissolve the hydrogen is high. Although th latent heat of fusion of tungsten is greater than that of platinu (as inferred from the value of ν_{max} of the Debye equation), it evidently incapable of dissociating the hydrogen to any measurab extent, for Sieverts has found the solubility of the gas to b exceedingly low. The determining factor in regard to th behaviour of the metal towards hydrogen would seem to be give by the product of the dielectric capacity and the latent heat. I respect of this product, the metals arrange themselves in th following order, commencing with the highest value of the product.

Ni, Al, Cu, Na, Fe, Pt, Zn, Ag.

It is evident that those metals which can dissociate or react with hydrogen possess the higher values for the product. In the case of nickel, we have no independent value of Φ, and therefore no value of D_0 independent of the solubility method made use of to calculate D. Its position in the series is therefore not significant.

When we compare the energy, represented by L, with the value of E_{H_2} we see that, especially at higher temperatures, more than one atom of the metal, in general two atoms, are required to contribute the energy necessary for dissociation of hydrogen. In the case of sodium at low temperatures, if we take the value for D_0, namely, 60, which is obtained from the resonance potential, we conclude that the energy required to dissociate one gram-molecule of hydrogen in sodium is $85,000/60 = 1420$ cals. Calculated for one gram-atom of hydrogen, the energy required is 710 cals., which is just capable of being furnished by the L term of sodium.

On the basis of the suggestion that the energy represented by the latent heat of fusion is the origin of the dissociation of hydrogen in metals, it would follow that the solubility of the gas

the molten metal should be considerably greater than in the d. This is in agreement with the experimental results of verts (*Zeitsch. physikal. Chem.*, 1911, **77**, 591), who has found .t at the melting point of the metal, the solubility of hydrogen molten copper is three times as great as it is in the solid, and .ce as great in molten nickel and iron as it is in the solid. rther, the increase of solubility with temperature is greater for molten than for the solid metal.

Variation of the Characteristic Potential of Metals with Temperature.

On the basis of the formula deduced for Φ, (equation [1]), it ιy be concluded that, in general, the greater the value of the ɔlectric capacity, the smaller the value of the characteristic ·tential. Since the dielectric capacity diminishes as the temperaıre rises, the value of Φ should increase slowly as the temperature ses. The effect of the variation of D_0 is, however, partly comɔnsated by the change in r_0. Owing to the temperatureɔefficient, it is not strictly correct to compare the calculated values Φ with those obtained from the photo-electric effect at the ·dinary temperature. The possible error in D_0 (which is obtained ·om the solubility of hydrogen in the metal) is such, however, s to render this objection less cogent. The temperature-coefficient the dielectric capacity of metals is distinctly less than that for on-metals.

Hydrogenation.

It is evident that the property possessed by certain metals of issolving hydrogen in the atomic form is closely related to the nown catalytic power of the same metals for the hydrogenation of nsaturated compounds. This view, which is no longer novel, was efinitely stated by Sieverts in 1910 as a result of his series of esearches, some of which have been considered in the preceding ›art of this paper. Although stress is thus laid on the fact of olubility of hydrogen in certain metals, it is not intended to dentify solubility itself with catalytic efficiency. The latter must lepend ultimately on obtaining hydrogen or other gases in the ιctive state, preferably the atomic state, at the surface of the netal. It is evident, however, that the property which enables ι metal to dissolve and to dissociate hydrogen will likewise cause ι similar activation of the gas at the surface, so that although .arge adsorbing surface is the necessary condition for the catalytic effect, the well-known specific influence of the metallic catalyst is

to be inferred from its capacity of dissolving and dissociating th gas. Nickel and cobalt, for example, in the finely divided form are known to occlude very much larger quantities of hydrogen than the same mass of metal in compact form (compare Sieverts *Zeitsch. physikal. Chem.*, 1907, **60**, 178), the effect being obviously an adsorption, the extent of which is dependent in turn on the specific nature of the metal, as indicated by its solvent power.

Among the numerous investigations of the mechanism of hydrogenation of unsaturated fats and oils, mention may be made of those recently carried out by Thomas (*J. Soc. Chem. Ind.*, 1920, **39**, 10T) and by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137, 322).

In connexion with the function of the catalyst (nickel), Thomas has applied the author's radiation hypothesis of chemical reactivity. The reaction is found to be unimolecular with respect to olein, and from the temperature-coefficient of the velocity-constant, corrected for the increase in solubility of the hydrogen in the metal with rise in temperature, Thomas has calculated that the critical increment amounts to 3820 cals. per gram-molecule of olein converted. This quantity is ascribed by Thomas entirely to the activation of the olein molecule. In view, however, of the numerical data obtained for the activation of hydrogen in nickel, it would appear necessary to deduct the energy required for the hydrogen. Thomas has found experimentally that the rate of the reaction varies as the 1·5 power of the hydrogen pressure in the apparatus, that is, three hydrogen atoms are required for one molecule of olein. The amount of energy required to dissociate one gram-molecule of hydrogen in nickel at 150° has been estimated in the present paper to be approximately 1700 cals. Consequently, to produce three gram-atoms, 2500 cals. are required. On subtracting this from the total critical increment obtained by Thomas, namely, 3820 cals., we obtain 1300 cals. as the critical increment of the olein. This quantity, expressed in terms of wave-lengths of radiation, corresponds with $21\,\mu$. Since the maximum of the temperature radiational energy at 150° occurs at about $7\,\mu$, it is evident that a considerable number of the olein molecules are activated to the required stage by the temperature of the system itself. That is, a catalyst is unnecessary for the activation of the olein.

In thus ascribing the energy term, 1300 cals., to the activation of the olein molecules, it is implied that diffusion has not to be taken into account. This is in agreement with the view put forward by Thomas, who remarks that the vigorous shaking to which

the olein–nickel mixture was subjected in his experiments excludes diffusion as a significant factor.

Thomas has made the remarkable discovery, already mentioned, that the rate of hydrogenation of olein is proportional to the pressure of the molecular hydrogen in the apparatus raised to the 1·5 power. It follows, as Thomas points out, that three atoms of hydrogen take part in the hydrogenation of one molecule of olein. The fact that this is an odd number is significant, as it involves the primary formation of a molecule midway in composition between olein and stearin. This half-saturated molecule possesses, necessarily, either one or three free valencies, which will cause the spontaneous formation of an apparently saturated bimolecular form having the composition $[C_3H_5(C_{18}H_{34}O_2)_3]_2$. The author is unaware whether any such intermediate stage has been observed. This bimolecular compound could, of course, decompose into a molecule of stearin and a molecule of olein.

Returning to the question of the temperature-coefficient, it may be pointed out that, on the above view, its numerical value should be considerably greater if copper were used as a catalyst in place of nickel. Thus, on the basis of the earlier considerations in this paper, we conclude that the amount of energy required to dissociate one gram-molecule of hydrogen in copper is of the order of 5000 cals. To produce three gram-atoms of hydrogen would require, therefore, 7500 cals. To this has to be added the energy of activation of olein, namely, 1300 cals., making in all a critical increment of 8800 cals. In the neighbourhood of 200°, it follows that the temperature-coefficient for an interval of 10° would be 1·21 (when corrected for the variation of the solubility of hydrogen in copper), whilst its value in the case of nickel is less than 1·13. At the same time, the velocity-constant with copper as catalyst would only be of the order 5×10^{-3} of the velocity with nickel.

It may be pointed out that the efficiency of nickel in respect of dissolving and dissociating hydrogen has been related to its dielectric capacity and the latent heat of fusion. This affords a certain amount of guidance in a search for a possibly more effective catalyst, which would probably be an alloy.

As regards the mechanism of hydrogenation, the first and essential stage would appear to be the formation of atomic hydrogen, this being accomplished by actual solution in, or by adsorption of, the gas on the surface of the metal. The second stage is to bring the olein molecule to the surface of the metal at which active hydrogen already exists. That is, collision of the olein (already activated in virtue of its temperature) with the

metal particle must take place. The final stage is the addition of atomic hydrogen at the moment of collision. These stages may be represented thus:

Hydrogen + nickel ⟶ atomic hydrogen available at the surface.
Olein molecule + nickel charged with hydrogen ⟶
collision ⟶ hydrogenation.

The fact that hydrogenation commences without a period of delay in such cases as olein indicates that the first stage, namely, production of atomic hydrogen, occurs rapidly. If the metal were completely covered by or united with the unsaturated compound before hydrogen was admitted, it would be impossible for hydrogenation to occur. This effect, "negative auto-catalysis," which is theoretically possible, evidently does not occur with olein and similar substances. In these circumstances, the measurable reaction which defines the rate of hydrogenation appears to be the second, namely, the rate of collision of the unsaturated compound with the catalyst. The collision frequency per c.c. per second of these two substances is given on the kinetic theory of gases by

$$\pi\sigma_1\sigma_2\sqrt{u_1^2+u_2^2}\,.\,N_{\text{Ni}}\,.\,N_{\text{olein}},$$

where σ_1 and σ_2 are the radii of the olein molecule and of the nickel particle, u_1 and u_2 the root-mean-square velocity of the olein molecule and the nickel particle, N_{Ni} the number of nickel particles per c.c., and N_{olein} the number of molecules of olein per c.c. Since the concentration of nickel is kept constant throughout any reaction, the above expression leads to a unimolecular velocity-constant.

The above expression, which gives the total number of collisions between nickel particles and olein molecules, does not allow for the fact that the resulting chemical change likewise depends on the critical increment term which defines the number of "favourable" collisions. The actual rate of the chemical process on the above basis would be given by

$$\pi\sigma_1\sigma_2\sqrt{u_1^2+u_2^2}\,.\,N_{\text{Ni}}\,.\,N_{\text{olein}}\;e^{-E/RT},$$

where E, obtained from Thomas's measurements, is 5576 cals. at 135° and 5228 cals. at 165°. These numbers are the fictitious values of E, which are obtained when no allowance is made for the change of the solubility of hydrogen in nickel with temperature. It is necessary to employ these values, and not the corrected value 3820 cals., when direct comparison with experimental velocity-constants is desired.

The number of favourable collisions, that is, the number of

nolecules of olein hydrogenated when expressed as a fraction of he total number of olein molecules present, is given by

$$\pi\sigma_1\sigma_2\sqrt{u_1^2+u_2^2}\,.\,N_{Ni}\,.\,e^{-E/RT},$$

vhich should be identical with the observed unimolecular velocity-onstant.

An attempt will now be made to apply this equation to the ıydrogenation of olein by finely divided nickel at 180°. At this emperature the value of E is 5000 cals. in round numbers. The uantity with which the largest error is likely to be associated is hat represented by σ_2, the average radius of the nickel particles. A quantity of finely divided nickel was examined under the micro-cope by Mr. L. E. Campbell in this laboratory. The sizes of the ifferent individuals varied greatly. On preparing a suspension f the same sample of nickel in glycerol, the coarsest particles fall ɔ the bottom, and, on withdrawing small quantities of the liquid t various levels and examining them, a more uniform appearance 'as obtained. It was found that the particles consisted in the ıain of individual units having a diameter of approximately $\times 10^{-4}$ cm., together with a smaller number of larger aggregates f approximately ten times this size, each aggregate having a orous structure, being apparently built up of the smaller units. Ve are probably justified, therefore, in employing the value $\times 10^{-4}$ as indicating the order of magnitnde of σ_2; it is impossible ɔ make a more exact estimate at the present time. Taking the ensity of nickel as 8·8, the mass of a single average nickel particle $4{\cdot}4\times10^{-9}$ gram. Hence, in the case of olein containing 1 per ənt. of nickel in suspension, the number of particles of nickel ər c.c. $=N_{Ni}=2\times10^{6}$. The mass of an olein molecule is 5×10^{-21} gram, which is extremely small compared with the mass a nickel particle. Consequently, we can neglect u_2, the velocity the metallic particle compared with u_1, the velocity of an olein olecule.

The term $\sqrt{u_1^2+u_2^2}$ becomes, therefore, u_1, which at 180° is ıual to $1{\cdot}1\times10^{4}$ cm. per second. The radius of the olein molecule known to be 6×10^{-8} cm. The term $e^{-E/RT}=3{\cdot}85\times10^{-3}$. ence

$$\pi\sigma_1\sigma_2u_1N_{Ni}e^{-E/RT} = 8\times10^{-3}.$$

ıe observed velocity-constant at $180°=3{\cdot}4\times10^{-4}$, time being pressed in seconds and natural logarithms being employed. The lculated value is therefore twenty-four times the observed. If were taken to be 10^{-3} cm. instead of 5×10^{-4} cm., the calculated locity-constant would be 2×10^{-3}, which is six times the observed. spite of the discrepancy, which may be well attributed to an

error in the size assumed for the nickel particle, for, according to the above expression, the velocity varies inversely as the square of the radius of the particle, the result might be regarded as prima facie evidence for the treatment of the problem on the basis of collisions. Velocity data with graded nickel of approximately uniform grain are apparently not available.

The above mechanism only requires collision between a single olein molecule and a single nickel particle, the latter being charged with atomic hydrogen. Of the total collisions, only a small fraction, namely, $e^{-E/RT}$, is effective for the chemical change. If permanent adsorption of olein as a result of collisions occurred, we should have expected a still higher velocity than that calculated, which already errs in the sense of being too high. True adsorption of the olein, therefore, apparently does not take place, the adsorption and solution phenomena being restricted to the nickel and hydrogen system. The absence of adsorption of the olein is in agreement with the results obtained by Armstrong and Hilditch on the hydrogenation of carbon monoxide to methane, although these authors regard the mechanism from a somewhat different point of view. Even when the concentration of the carbon monoxide is small, the effect takes place in the presence of olein, and, "moreover, the amount of change is as much, if not more, than the amount which takes place under similar conditions in absence of oil." Naturally, the nature of the unsaturated substance, olein, linolein, etc., determines the rate of the reaction, since the total critical increment, E, contains a term characteristic of the substance undergoing change. This is in agreement with one of the conclusions drawn by Armstrong and Hilditch. Further, since cotton-seed oil, linseed oil, whale oil, and olive oil contain more than one unsaturated substance, this introduces a change in the value of E during the course of a given reaction. In the case dealt with above, however, Thomas has determined the velocity-constants of the two constituents of olive oil, olein and linolein, and the collision equation has been applied to the single substance olein, as this forms 90 per cent. of olive oil, and presumably the data obtained for this substance are the most trustworthy.

The mechanism of hydrogenation assumed as a working hypothesis in the foregoing paragraphs involves essentially the dissociation of hydrogen, either adsorbed on or absorbed by the nickel, followed by collisions between the charged nickel particles and the unsaturated molecules. It is not intended to suggest that in all cases collision frequency is the determining factor. It appears to be so in the case of olein, and presumably of similar substances. In other cases there is the possibility of adsorption of

the unsaturated substance. In the latter cases, the observed rate of reaction would be expected to be considerably greater than that given by the collision equation, the degree of applicability of the expression being made use of as a criterion for the absence or presence of adsorption. Either view would also lead us to expect dehydrogenation of a saturated compound in the absence of hydrogen, since nickel will tend to abstract hydrogen from the compound in order to attain an equilibrium between hydrogen, unsaturated substance, and saturated substance. Under ordinary conditions of hydrogenation, in which hydrogen is used in large excess, the equilibrium point is necessarily shifted far to one side. For those cases to which the collision expression applies, the equilibrium-constant would be expected to take the form:

$$\frac{\text{equilibrium concentration of unsaturated compound} \times \text{concentration of charged Ni}}{\text{concentration of saturated compound}}$$

that is, the equilibrium *constant* would not depend on the amount of nickel present in the system. If, on the other hand, adsorption is a significant term, the above equilibrium expression is meaningless. In either case, we should expect that the best hydrogenating agent would likewise be the best dehydrogenating agent.

Summary.

(1) *From a consideration of the solubility of hydrogen in certain* metals, it is inferred that metals in general possess finite dielectric capacities.

(2) Values for the dielectric capacities of a number of metals at various temperatures have been obtained from the critical increments of dissociation of hydrogen dissolved therein, by making use of the fact that 85,000 cals. per gram-molecule is the critical increment of dissociation of hydrogen in the free, gaseous state.

(3) The insolubility of hydrogen in certain metals is regarded as being due to the inability of these metals to dissociate the gas. For this reason, these metals may be expected to function as negative catalysts when deposited on the surface of active metals in hydrogenation.

(4) An expression has been obtained for the characteristic potential at the surface of a pure metal, namely,

$$\Phi = \frac{e}{r_0 \log_e D_0}\left(1 - \frac{1}{D_0}\right),$$

where e is the charge on an electron, r_0 the average distance of an electron from its neighbouring ion in the metal, and D_0 is the

dielectric capacity of the metal. This expression is found to be in satisfactory agreement with the accepted values of Φ, the latter being obtained from thermionic effects, the threshold frequency of the normal photo-electric effect, and the resonance potential of metallic vapours. This agreement is regarded as supporting the view of the existence of finite dielectric capacities in the case of metals. By means of the above equation, it is calculated that Φ for nickel is 2·8 volts. The contact potential difference between two pure metals is necessarily the difference of their Φ values.

(5) In addition to the dielectric capacity, it is shown that the dissociating power of a metal for hydrogen depends on the existence in the metal of radiation of a sufficiently short wave-length. This is shown to be related to the magnitude of the atomic latent heat of fusion of the metal, a measure of the dissociating power being given by the product of the dielectric capacity and the latent heat of fusion.

(6) In the light of the foregoing conclusions, the mechanism of hydrogenation of olein by nickel and other metals is considered, the processes involved consisting primarily of the dissociation and solution or adsorption of hydrogen by the particles of the metal with which the olein molecules, which are already activated in virtue of their temperature, collide. It is found that a simple collision expression of the following form reproduces, in so far as order of magnitude is concerned, the observed unimolecular velocity-constants obtained by Thomas (*loc. cit.*):

$$k = \pi\sigma_1\sigma_2 u_1 N_{\mathrm{Ni}} e^{-E/RT},$$

where σ_1 is the mean radius of the olein molecule, σ_2 the corresponding quantity for an average particle of nickel, u_1 the mean thermal velocity of the olein molecule, and E is the uncorrected critical increment of the reaction, that is, the critical increment observed directly by experiment, uncorrected for the variation with temperature of the solubility of hydrogen in the metal. It is concluded that, in the case of hydrogenation of olein and of similar substances, adsorption of the unsaturated compound on the metal does not take place, the adsorption being restricted to the metal–hydrogen components.

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LXVII.—*The Preparation of* cyclo*Heptane*-1 : 1-*di-acetic Acid.*

By James Nelson Edmund Day, George Armand Robert Kon, and Arnold Stevenson.

In two recent papers (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080; Ingold and Thorpe, T., 1919, **115**, 320), a comparison was made between derivatives of $\beta\beta$-dimethylglutaric (I) and *cyclo*-

$$CH{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}\quad\text{(II.)}\qquad \begin{matrix}Me\\Me\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}\quad\text{(I.)}$$

hexanediacetic acid (II) with respect to the degree of ease with which a bond can be established between the two α-carbon atoms of the acid, and the stability of the trimethylene compounds so produced.

From the experimental data, it is argued that the forcing apart of two of the valencies of the quaternary carbon atom from 109°28′ to 120°, consequent on the formation of a *cyclo*hexane ring, has the effect of diminishing the angle between the other two valencies, thus bringing the two $\cdot CH_2{\cdot}CO_2H$ groups attached to the quaternary carbon atom into closer proximity. This facilitates the closing of a trimethylene ring, and, moreover, the

$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}\qquad CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH{\cdot}CO_2H\\|\\CH{\cdot}CO_2H\end{matrix}$$

spiro-compound so produced is more stable than the corresponding trimethylene derivative, caronic acid (III).

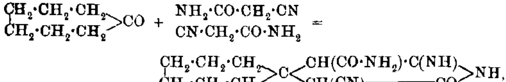
$$\begin{matrix}Me\\Me\end{matrix}{>}C{<}\begin{matrix}CH{\cdot}CO_2H\\|\\CH{\cdot}CO_2H\end{matrix}\quad\text{(III.)}\qquad \begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\|\\CH_2{\cdot}CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}\quad\text{(IV.)}$$

It is obvious that this effect should be even more marked in the case of a compound in which two of the valencies of the quaternary carbon atom are forced still farther apart by participating in the formation of a seven- or eight-membered ring, the angle in these cases being, according to Baeyer's strain theory, 128°34′ and 135° respectively.

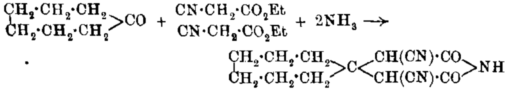
The interest attaching to the question has led the present authors to study the best conditions for the preparation of *cyclo*-

heptanediacetic acid (IV), which would serve as the starting point in an investigation of the problem.

From analogy to similar acids containing five- or six-membered rings, it was thought that the desired acid could be readily obtained by condensing suberone with cyanoacetamide by Thole and Thorpe's method (T., 1911, **99**, 422) and hydrolysing the product, or with ethyl cyanoacetate and ammonia in alcoholic



solution by Guareschi's method (compare Kon and Thorpe, T.,



(V.)

1919, **115**, 686), the latter product being also readily hydrolysed to the acid.

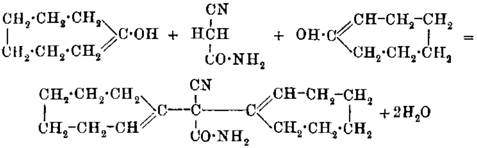
The necessary quantity of suberone was therefore prepared, but it was found that this ketone failed to react with cyanoacetamide under the conditions used by Thole and Thorpe in similar cases.

Guareschi's method was therefore adopted, but it was found that a yield of scarcely 15 per cent. of the theoretical was the best that could be obtained under the different conditions tried, and it generally amounted to about 10 per cent. only.

The reason of the unsatisfactory yields is at present without explanation. It may be due to the solubility of the ammonium salt of the dicyano-imide, which is not precipitated from the alcoholic solution, as is the case in other condensations of a similar nature; but it is also conceivable that the effect of a seven-membered ring may be to inhibit the closing of a piperidine ring, in the same way and for the same reason as it may be expected to facilitate the formation of a three-membered ring, that is, by reducing the angle between the two valencies of the quaternary carbon atom which do not take part in the formation of the seven-membered ring.

An examination of the mother liquor from the original condensation has led to the discovery, in addition to cyanoacetamide and unchanged ketone, of a compound apparently formed from one molecule of the former and two molecules of the latter by the

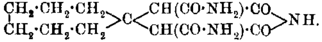
elimination of two molecules of water, doubtless in accordance with the following scheme:



(VI.)

although the experimental data are as yet insufficient to establish the constitution with certainty.

An examination of the main condensation product showed that it was formed in the usual manner from one molecule of the ketone reacting with two molecules of cyanoacetamide (see p. 640). It possessed the usual properties of such compounds, crystallised well, and gave on treatment with cold concentrated sulphuric acid the diamide,



(VII.)

On complete hydrolysis by means of boiling 85 per cent. sulphuric acid, a fair yield of cyclo*heptanediacetic acid* was obtained from the imide.

The acid, which melts at 156—157°, greatly resembles its homologues, *cyclo*hexanediacetic acid (Thole and Thorpe, *loc. cit.*, p. 445) and *cyclo*pentanediacetic acid (Kon and Thorpe, *loc. cit.*, p. 700), and was characterised by the formation of its *anhydride* and *semianilide*, which crystallise very readily.

Experimental.

Preparation of Suberic Acid.

Markownikov's method (*Ber.*, 1894, **26**, 3089) was followed. One hundred kilos. of dilute nitric acid (D 1·25) were gradually added to 50 kilos. of castor oil contained in a large steam-jacketed pan; each addition of the acid caused considerable frothing, so that the operation occupied several days; the contents of the pan were finally heated for another day.

The aqueous layer was then syphoned out, and the gummy oil repeatedly extracted with boiling water. The combined aqueous solutions were evaporated to dryness, yielding about 5 kilos. of a dark solid still contaminated with oily matter.

The whole quantity was purified by dissolving it in water, boiling with animal charcoal (500 grams of crude acid, 750 c.c. of water, and 40 grams of animal charcoal), rapidly filtering, and allowing to crystallise. The solid so obtained was sandy in appearance and melted indefinitely between 110° and 130°; the quantity was 3000 grams, which includes some recovered by extracting the charcoal with hot water.

Preliminary experiments showed that Markownikov's method of separating suberic and azelaic acids by means of ether (*loc. cit.*) was extremely tedious and unsatisfactory, and an attempt was made to find a simpler method. This was ultimately achieved enabling sufficiently pure suberic acid to be produced in one operation.

Three hundred grams of mixed acids, purified as above, are suspended in 1500 c.c. of boiling benzene and brought into solution by adding absolute alcohol (about 390 c.c. were usually required). On cooling, almost pure suberic acid, melting at 136—138°, separates out, and can be used for the preparation of suberone without further purification.

A second crystallisation is sufficient to give pure, although still somewhat coloured, suberic acid, melting at 139—140° (Found: C=55·01; H=7·83. $C_8H_{14}O_4$ requires C=55·18; H=8·05 per cent.).

The separation of the acid was usually hastened by leaving the vessel in a cool place overnight, and it was found that the yield varied somewhat with the temperature, but was usually about 120 grams; if it was much higher, the quality of the product was inferior.

The mother liquors from the first crop of suberic acid were evaporated to half their bulk and allowed to crystallise again; from the solid which separated, more suberic acid could be obtained by repeating the process described above. The total amount of suberic acid produced in this way was 1500 grams.

The combined mother liquors on evaporation yielded a residue, from which, after removing the oily impurities by rubbing twice with dry ether and pressing on porous plates, azelaic acid could be obtained in a state of purity by repeated crystallisation from water (m. p. 106°; Found: C=57·42; H=8·30. $C_9H_{16}O_4$ requires C=57·44; H=8·51 per cent.), but the quantity was rather small (200 grams).

Preparation of Suberone.

The catalytic process of the Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 256622), which was found to give such excellent

results in the case of adipic acid (Kon and Thorpe, *loc. cit.*), could not be applied to suberic acid, the latter distilling unchanged; the modification involving the use of iron filings instead of baryta as a catalyst was also unsatisfactory. The following method was finally adopted.

The suberic acid was converted through its ammonium salt into the calcium salt, using a 20 per cent. excess of lime. The salt was carefully dried at 100° and distilled in portions of not more than 28 grams at a time.

The best vessel for the purpose was found to be a 500 c.c. conical flask suspended in an iron saucepan serving as an air-bath, and provided with an asbestos cover perforated to allow the neck of the flask to protrude.

The flask was provided with a cork with two tubes passing through. One of these enabled a current of an inert gas to be circulated through the apparatus, whilst the other, which penetrated half way down into the flask and consisted of capillary tubing (compare Young, T., 1891, **59**, 621), served as a still-head, and was connected to the condenser. This arrangement minimises the decomposition, which is caused by the distillate dropping back on to the hot calcium salt in the flask.

Four such sets of apparatus enabled 1400 grams of suberic acid to be worked up in a few days.

The crude distillate was separated from the small amount of water and fractionated, the fractions obtained from the total amount of suberic acid being as follows:

(1).........	Below 100°	8 grams
(2).........	100—160°	15 ,,
(3).........	160—174	21 ,,
(4).........	174—183	362 ,,
(5).........	183—190	31 ,,
(6).........	190—200	26 ,,
(7).........	200—240	20 ,,

Fraction (4) was pure enough to condense with ethyl cyanoacetate. An attempt was made to purify fraction (5) through the semicarbazone, but this led to loss; the bisulphite method, however, proved very satisfactory, and a further 50 grams of pure suberone were obtained from the fractions of high and low boiling points.

Condensation of Suberone with Ethyl Cyanoacetate: ω-Imide of $\alpha\alpha_1$*-Dicyanocycloheptane-1:1-diacetic Acid* (V, p. 640).

As already mentioned in the introduction, only a very poor yield of the above condensation product could be obtained by the Guareschi method, and the ketone, which had failed to react, had to be recovered by a long and tedious process.

The best results were obtained as follows: 44 grams of suberone,

90 grams of ethyl cyanoacetate, and 200 c.c. of saturated alcoholic ammonia were mixed and kept in a stoppered bottle for three days. The mixture deposited a certain amount of cyanoacetamide and assumed a deep yellow colour. It was mixed with about 800 c.c. of water, and the aqueous layer twice extracted with ether and acidified, when 11 grams of a crystalline solid were precipitated, and 1·5 grams were recovered by evaporating the mother liquor to half its bulk.

On recrystallisation from dilute alcohol, the compound is obtained in colourless, sparkling plates melting at 203·5—204°:

0·1133 gave 0·2637 CO_2 and 0·0646 H_2O. C=63·71; H=6·34.
0·1045 ,, 15·95 c.c. N_2 at 19·5° and 757·7 mm. N=17·38.
$C_{13}H_{15}O_2N_3$ requires C=63·64; H=6·17; N=17·14 per cent.

*ω-Imide of $αα_1$-Dicarbamyl*cyclo*heptane-1 : 1-diacetic Acid* (VII, p. 641).

If the above dicyano-imide is dissolved in ten times its weight of cold concentrated sulphuric acid, and the solution, after remaining for twenty-four hours, is poured on ice, a crystalline solid is gradually deposited. It forms transparent prisms blackening at 295° and decomposing without melting at about 305°:

0·0914 gave 11·9 c.c. N_2 at 19·5° and 765·6 mm. N=14·98.
$C_{13}H_{19}O_4N_3$ requires N=14·94 per cent.

It is very sparingly soluble in all solvents, but can be recrystallised from a large quantity of acetic acid.

cyclo*Heptane-1 : 1-diacetic Acid* (IV, p. 639).

Twenty grams of the dicyano-imide are dissolved in 70 c.c. of concentrated sulphuric acid, 15 c.c. of water are added, and the solution is gently heated on a sand-bath until a vigorous evolution of carbon dioxide begins; the temperature is then kept steady for about an hour until the reaction slackens, when the liquid is allowed to cool; 50 c.c. of water are then added, and the solution is boiled under reflux for five hours. When cold, the solution is diluted with water and repeatedly extracted with ether, the acid being removed from the ether by shaking with sodium carbonate solution; it is precipitated when the latter is acidified (13·5 grams).

The acid obtained in this way crystallises well from dilute alcohol in long, flattened needles, which melt at 156—157°. It is very sparingly soluble in water or benzene, differing in the latter property from the isomeric methyl*cyclo*hexanediacetic acids, which are appreciably more readily soluble in benzene:

0·1282 gave 0·2902 CO_2 and 0·0980 H_2O. C=61·73; H=8·49.
$C_{11}H_{18}O_4$ requires C=61·64; H=8·46 per cent.

A neutral solution of the ammonium salt of the acid gives no precipitate with a normal solution of barium chloride. With calcium chloride, a precipitate is obtained on boiling the solution, and this does not redissolve on cooling or adding water.

The *silver* salt is obtained as a curdy precipitate on adding a solution of silver nitrate to a neutral solution of the ammonium salt. It is very sparingly soluble:

0·3025 gave 0·1515 Ag. Ag = 50·08.

$C_{11}H_{17}O_4Ag$ requires Ag = 50·42 per cent.

The *anhydride* is readily formed by the action of boiling acetyl chloride on the acid, and crystallises in large laminæ as the reagent evaporates. It separates from light petroleum (b. p. 60—80°) in iridescent plates melting at 75—76°, and is slowly reconverted to the acid on boiling with water:

0·1189 gave 0·2940 CO_2 and 0·0883 H_2O. C = 67·41; H = 8·25.

$C_{11}H_{16}O_3$ requires C = 67·35; H = 8·22 per cent.

The *semianilide* is prepared by boiling a benzene solution of the anhydride with aniline for a few minutes. It crystallises on evaporating off the benzene, and can be purified by recrystallisation from dilute alcohol. It forms small plates melting at 139·5—140°:

0·1321 gave 0·3409 CO_2 and 0·0957 H_2O. C = 70·37; H = 8·05.

$C_{17}H_{23}O_3N$ requires C = 70·53; H = 8·01 per cent.

The *imide* of cyclo*heptanediacetic acid*,

$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2 \\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CO \\ CH_2\cdot CO\end{matrix}\!>\!NH,$$

is formed as a by-product in the hydrolysis of the dicyano-imide, and can be obtained by evaporating the ether used for extracting the acid after the latter has been removed by means of sodium carbonate solution. The solid residue crystallises extremely well from benzene, and is obtained in large, iridescent plates melting at 177—178·5°:

0·1202 gave 8·0 c.c. N_2 at 20·0° and 757·1 mm. N = 7·55.

$C_{11}H_{17}O_2N$ requires N = 7·18 per cent.

Examination of the Mother Liquors from the Original Condensation (Compound VI, p. 641).

The ethereal extract containing unchanged suberone is reduced to a small bulk by distillation on a steam-bath, using an efficient fractionating column to prevent loss of ketone. The residue in the flask is treated with a concentrated solution of sodium hydrogen sulphite, which rapidly combines with the ketone; the solid compound is isolated by filtration, purified by grinding with ether, and

yields, on decomposition with alkali, the ketone in a state of purity; about one-fifth to a quarter of the original amount is recovered in this way.

The ethereal washings are added to the filtrate from the hydrogen sulphite compound, which contains mainly cyanoacetamide, in addition to oily impurities. On prolonged keeping, a small quantity of a very sparingly soluble solid separates, and can be purified by recrystallisation from much alcohol, separating from this solvent in prisms melting at 187°:

0·1367 gave 0·3745 CO_2 and 0·1078 H_2O. C=74·71; H=8·76.
0·1581 ,, 14·8 c.c. N_2 at 22·0° and 748·8 mm. N=10·40.
$C_{17}H_{24}ON_2$ requires C=74·94; H=8·89; N=10·29 per cent.

On boiling for ten minutes with concentrated hydrochloric acid, this compound is transformed into a semi-solid mass which solidifies on cooling. On crystallisation from dilute alcohol, this is obtained in small plates melting sharply at 137°. It is much more readily soluble in alcohol than the former compound, with which it is isomeric:

0·1482 gave 0·4973 CO_2 and 0·1159 H_2O. C=74·94; H=8·69.
0·1606 ,, 14·6 c.c. N_2 at 21·3° and 775·2 mm. N=10·46.

These compounds are still under investigation.

In conclusion, our best thanks are due to Prof. J. F. Thorpe, F.R.S., for his interest in the course of the investigation; we are indebted to Messrs. May and Baker, Ltd., of Battersea, for having undertaken the preparation of crude suberic acid from which our suberone was prepared; and to Mr. E. A. Perren, of this College, for his help in the purification of suberic acid.

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South Kensington. [Received, April 28th, 1920.]

LXVIII.—*Estimation of Nitroform by Potassium Permanganate.*

By Phyllis Violet McKie.

A simple and accurate method of estimating nitroform in the presence of nitric, nitrous, and sulphuric acids when titration by alkali hydroxide (Hantzsch, *Ber.*, 1899, **32**, 628) is not applicable is found in the reduction of permanganate in acid solution (compare Orton and McKie, this vol., 283).

$$CH(NO_2)_3 + 2O_2 + H_2O = CO_2 + 3HNO_3$$

That this equation quantitatively represents the reaction was confirmed by determining the nitric acid (by oxidation by ferrous salt in an atmosphere of carbon dioxide) produced from given quantities of nitroform and potassium permanganate. Thus it was found that 1 mole of potassium nitroform ($CK[NO_2]_3 = 189{\cdot}15$) reduced (i) 79·84, (ii) 79·96, (iii) 79·95 litres of *N*/10-permanganate, and yielded (i) 2·997, (ii) 2·990, (iii) 2·995 moles of nitric acid.

To ascertain the best procedure and to test the accuracy of the method, standard solutions were made up of the pure potassium and ammonium salts, which were prepared from pure tetranitromethane by the methods, respectively, of Hantzsch (*loc. cit.*) and Pictet and Genequand (*Ber.*, 1903, **36**, 2228), and recrystallised by slowly evaporating their aqueous (alkaline in the case of the ammonium salt) solutions at the laboratory temperature over sodium hydroxide under diminished pressure, and shielded from light.

The volumetric procedure, which was found to give the best results, is as follows. After ascertaining roughly the volume of permanganate which is required by some volume of the given nitroform solution, 25 c.c. of the latter are added to a known excess (50 c.c.) of *N*/10-permanganate acidified with 10 c.c. of 10 per cent. sulphuric acid. The mixture is then heated to 30°; after remaining for one minute at that temperature, 20 c.c. of a 2·5 per cent. solution of potassium iodide is added, and the liberated iodine titrated with *N*/10-thiosulphate, using starch-paste as indicator.

As the reaction is rather slow, both considerable excess of permanganate and the elevated temperature (30°) are essential; extension of the time or a higher temperature is not permissible, owing to a separation of manganese dioxide which then occurs. Failure to oxidise the whole of the nitroform is indicated by a persistent yellow colour after the titration of the iodine.

In nitration products, titration in the manner described results in a reduction of the permanganate equivalent both to the nitroform and to the "nitrous acid" (compare Lunge, "Sulphuric Acid and Alkali," 4th ed., 1913, **1**, i, 388). To determine the nitroform, the mixture may first be titrated, then the "nitrous acid" removed (partly) by aspiration, and the mixture again titrated. It is found that at a given temperature and with a given air current, the percentage loss of nitrous acid is independent of the initial concentration within wide limits. Thus, at 16°, with an air current of 0·1 litre per minute, it was found that 73·3 (72·8—73·[illegible] per cent. of the nitrous acid disappears in one hour

from solutions containing nitric acid (7—8 per cent.), nitroform, and nitrous acid.

An alternative method is the destruction of the "nitrous acid" by ammonium nitrate (compare Gailhat, *J. Pharm. Chim.*, 1900, [vi], **12**, 9, and Gerlinger, *Zeitsch. angew. Chem.*, 1902, **14**, 1250, both of whom used ammonium chloride). The substitution of carbamide for the purpose leads to a small (8—10 per cent.) loss of nitroform.

To a solution of nitroform containing 0·2—0·3 gram of nitrous acid, 3 grams of ammonium nitrate are added; the mixture, which should not be alkaline, is boiled for a short time (one minute suffices), cooled to 30°, and titrated with permanganate. That the destruction of the nitrous acid is complete can be shown by potassium iodide, a reagent which is not affected rapidly by nitroform. The table illustrates the results of experiments in which nitrous acid was removed by ammonium nitrate.

$CK(NO_2)_3$. Gram.	$NaNO_2$. Gram.	$N/10$-$KMnO_4$. Nitroform. C.c.	$CK(NO_2)_3$ found. Gram.	$CK(NO_2)_3$ found. Percentage.
0·03004	0·04	12·7	0·03994	100·0
0·03004	0·04	12·67	0·02995	99·72
0·03004	0·02	12·7	0·03004	100·0
0·03004	0·02	12·69	0·03000	99·86
0·03004	0·06	12·75	0·03012	100·3
0·03004	0·06	12·72	0·03007	100·1

As an alternative, the nitroform may be distilled in a current of steam from the product (100 c.c. acidified with 15 c.c. of phosphoric acid, D 1·7), after treatment with ammonium nitrate, and the distillate titrated. About thirty minutes are required for the nitroform to pass over.

Comparisons of the above method have been made with titration by alkali of the nitroform extracted by ether (in the absence of nitrous acid), or distilled in a current of steam, and also with a method based on the precipitation by nitron (Schmidt, *Ber.*, 1919, **52**, [*B*], 400), which appeared while this investigation was in progress. The permanganate method is far more convenient, and, by comparison of the two methods, more accurate.

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LXIX.—*The Action of Alcohol on the Sulphates of Sodium.*

By Gerald Snowden Butler and Horace Barratt Dunnicliff.

The literature dealing with the solubility relationships of the sulphates of sodium is given by Foote (*J. Ind. Eng. Chem.*, 1918, **10**, 896), and Saxton (*ibid.*, 897) draws certain important conclusions relating to the composition of the solid sulphates of sodium prepared according to a method by which these were washed first with a mixture of sulphuric acid, water, and alcohol, then with alcohol, and finally with ether.

The present paper shows (1) that sodium sulphate and sodium hydrogen sulphate are acted on by a mixture of alcohol and sulphuric acid, and (2) that the washing with alcohol would decompose sodium hydrogen sulphate alone or in the presence of sodium sulphate, but would not decompose the compound $Na_2SO_4,NaHSO_4$. Saxton does not state how many times his compounds were washed with alcohol or ether, or if the washing was continued until the washings were neutral. It is shown below that, with or without preliminary washings with alcohol, many days' extraction with ether are required completely to remove the acidity from sodium sulphate or hydrogen sulphate which has been treated with alcoholic sulphuric acid. This point appears to be of great importance in connexion with the results given in Saxton's paper.

Lunge ("Sulphuric Acid and Alkali," 1909, Vol. II, Part I, 29) states that the compound $Na_3H(SO_4)_2$, observed by Thomson and Mitscherlich, is stable in air (see also D'Ans, *Ber.*, 1906, **39**, 1534), that (*loc. cit.*, p. 24) water decomposes sodium hydrogen sulphate into neutral sulphate and free sulphuric acid (compare Pascal and Ero, *Bull. Soc. chim.*, 1919, [iv], **25**, 25), and that alcohol deprives powdered sodium hydrogen sulphate of all free acid (see also Roscoe and Schorlemmer's "Treatise on Chemistry," 1913, Vol. II, pp. 261 and 341, where a similar statement is made regarding potassium hydrogen sulphate).

Pascal and Ero (*loc. cit.*) have studied the ternary system Na_2SO_4–H_2SO_4–H_2O. They state that a fused mixture of sodium sulphate and hydrogen sulphate is converted on cooling through 179° into the compound $Na_2SO_4,NaHSO_4$. Further, that nitre-cakes having an acidity inferior to 36 per cent. of sulphuric acid, on cooling after the retort is tapped, must pass through that temperature, and must therefore consist of a mixture of sodium hydrogen sulphate and the compound $Na_2SO_4,NaHSO_4$.

EXPERIMENTAL.

This work was undertaken as part of a research on the recovery of sulphuric acid from nitre-cake by means of spirits of wine (commercial ethyl alcohol). Experiments on commercial nitre-cakes were somewhat anomalous, but showed that nitre-cake, whether dry or moistened with 10 per cent. of water, when washed with either commercial (undried) alcohol or with absolute alcohol gave a residue having an acidity corresponding with about 18·7 per cent. of sulphuric acid, and that even in cases where the water added to the nitre-cake was as much as 60 per cent. of the weight of the cake, the residue had an acidity of about that value.

In view of the statements mentioned above regarding the action of alcohol on sodium hydrogen sulphate, it was expected that the residues resulting from these experiments would be free from acid. The fact that they invariably showed an acidity approximating to 18·5 per cent. suggested the formation of an acid salt having an acidity inferior to that of sodium hydrogen sulphate. The subsequent work was undertaken with the object of elucidating this point.

It is now known, as the result of this work, that exhaustive extraction of nitre-cake by commercial alcohol containing even small percentages of water leads to the progressive diminution in the acidity of the residue after each extraction, and finally results in complete extraction of the acid. The constancy of the value (about 18·5 per cent.) obtained in the above experiments is due to the fact that the residues were not washed exhaustively with alcohol. Washing with the alcohol was only repeated four or five times. The progressive extraction of nitre-cake by commercial spirit has been studied by the authors, and the acidity in the residue after each extraction has been determined. Full details of this part of the work will be published in a subsequent paper on the commercial aspect of the subject, but the values given in table I will illustrate the points sufficiently for the present purpose, and will explain one of the several reasons why an investigation of the subject with pure materials was undertaken.

TABLE I.

Successive Extraction of Nitre-cake by Moist Alcohol. (About 5 per cent. of Water.)

	Sulphuric acid. Per cent.
Acidity of original cake	33·0
Acidity of residue after 6th extraction with alcohol...	16·4
,, ,, 12th ,, ,, ...	8·8
,, ,, 18th ,, ,, ...	1·6

It will be shown that pure, dry alcohol extracts acid from pure sodium hydrogen sulphate until the residue contains only 18·69 per cent. (calc.: 18·7 per cent.) of acidity as sulphuric acid, and that neither in the cold nor when heated has dry alcohol any further action on it.

The results quoted for commercial nitre-cake were obtained because the solid, that is, the nitre-cake or partly extracted nitre-cake, was not washed until the washings were neutral. In fact, the above results (table I) show that, with commercial spirits of wine, a neutral washing could not have been obtained until all the acidity had been extracted from the cake.

Preparation of Materials.—Sodium sulphate was prepared by neutralising a solution of pure sodium carbonate with pure sulphuric acid. The solution was evaporated to dryness and fused until neutral.

Sodium hydrogen sulphate, prepared from the calculated quantities of pure sodium carbonate and pure sulphuric acid, was fused at 200° until no further loss was observed. The salt is hygroscopic. It gave the following analysis:

	Found. Per cent.	Calc. Per cent.
Free acid as H_2SO_4	40·76	40·83
Sodium sulphate formed on ignition	59·10	59·18
"SO_4" as Na_2SO_4	39·80	40·00
"SO_4" estimated as $BaSO_4$	67·60	67·53

In all experiments in which pure, dry sodium sulphate of hydrogen sulphate was used, the sulphate was fused and poured into a hot agate mortar, quickly ground up as soon as solidification had set in, and transferred to a weighing bottle.

Sulphuric acid (100 per cent.) was prepared by mixing calculated quantities of pure sulphuric acid with fuming sulphuric acid. The strength was 100·38 per cent., and the concentration was reduced to 100·10 per cent. by exposure to a moist atmosphere.

Ethyl Alcohol.—Pure absolute alcohol was left in contact with lime for several days and then distilled. This operation was repeated until the strength of the distillate, as determined from its density, was 99·80 per cent. by weight.

Alcoholic sulphuric acids were made up by mixing refined alcohol with 100 per cent. sulphuric acid. The approximate strength was obtained by weighing, and the actual strength was determined by titration. Esterification takes place slowly (at 18—19°), and at that temperature about three weeks are required for equilibrium to be established. The percentage "total" acidity, *x*, is found by evaporating a weighed portion of the alcoholic sulphuric acid to pastiness with excess of standard sodium or potassium hydroxide, and then heating in an air-oven for half

an hour at 120°. This ensures complete decomposition of the ethyl hydrogen sulphate. The percentage acidity by direct titration, b, is found by titrating a known weight of the alcoholic sulphuric acid with standard alkali hydroxide. The percentage esterification of the sulphuric acid present is given by

$$\frac{2(a-b)}{a} \times 100.$$

These values (see figure and tables V and VI) have been carefully verified. They differ considerably from those previously available. This work on ethyl hydrogen sulphate will be the subject of a subsequent paper.

Ethyl Ether.—Commercial "pure" ether was dried over calcium chloride, then by exposure to metallic sodium with intermittent shaking, and was finally distilled from sodium.

The Action of Pure, Dry Alcohol on Pure, Dry Sodium Sulphate and its Crystalline Hydrates.

Alcohol has no action on neutral, anhydrous sodium sulphate. Sodium sulphate is sparingly soluble in dilute alcohol.

When the sulphates $Na_2SO_4,10H_2O$ and $Na_2SO_4,7H_2O$ are treated with dry, cold alcohol, the whole of the water of crystallisation is extracted and the anhydrous sulphate remains. When a supersaturated solution of sodium sulphate in water is treated with warm alcohol (D 0·850), the heptahydrate crystallises out (Löwel, *Ann. Chim. Phys.*, 1851, [iii], **33**, 334; 1857, **49**, 32).

The Action of Pure, Dry Alcohol on Pure, Dry Sodium Hydrogen Sulphate.

The first experiments were carried out with ordinary "absolute" alcohol not specially dried. The dried, powdered hydrogen sulphate was shaken for a short time with excess of this alcohol, filtered, and then washed repeatedly with the same substance. The acidity of the residue fell rapidly to about 18·7 per cent. of sulphuric acid, the washings being strongly acid, and then continued to fall, but very slowly, and the washings were only faintly acid. Two samples, after very exhaustive washing, contained acidities of 17·53 and 17·46 per cent. respectively, and the washings still showed faint acidity. The experiments were repeated with specially dried alcohol prepared as described above, and similar results were obtained. The acidity, as before, rapidly fell to about 18·7 per cent., and then decreased very slowly, but in this

case exhaustive washing reduced the acidity only to 18·07 per cent. and 18·31 per cent. in duplicate samples.

Now, an acidity of 18·7 per cent. corresponds with that of the intermediate sulphate, $Na_2SO_4,NaHSO_4$, and it was concluded that the rapid reduction of the acidity to approximately this value was due to the formation of this salt. It was further concluded that the reduction of the acidity below 18·7 per cent. was due to water in both cases. The method of extraction on an open filter favoured the absorption of atmospheric moisture by the alcohol.

Attempts to eliminate the effect of atmospheric moisture by carrying out the extraction in a Soxhlet apparatus produced similar results; prolonged extraction invariably gave a residue having an acidity slightly below 18·7 per cent. In this case, it was decided that water from another source was responsible, partly, at any rate, for the anomalous results. It has been shown repeatedly in the course of this work that ethyl hydrogen sulphate is invariably formed when alcohol acts on sodium hydrogen sulphate, and t follows that an equivalent quantity of water must be present as a result of this reaction.

$$3xNaHSO_4 + yEtOH = EtHSO_4 + xNa_2SO_4,NaHSO_4 + H_2O + (x-1)H_2SO_4 + (y-1)EtOH.$$

In an extraction in a Soxhlet apparatus, this water would dilute he alcohol and would distil over with it, and the effect would be he same as that produced by the undried alcohol in the method f extraction by washing on a filter. Attempts were made to liminate this water by placing in the flasks of the extraction pparatus (1) anhydrous copper sulphate, and (2) magnesium owder, the latter in the hope that magnesium sulphate and ydrogen would be formed and the production of ethyl hydrogen ulphate prevented. Both failed, owing to the difficulties in carryng out the extraction, caused mainly by violent bumping in the ask. It was finally decided that the best method of attacking he problem was to allow an excess of dried alcohol to remain in ontact with the salt for a time sufficient to permit of equilibrium eing reached, and then to remove the liquor from the sphere of tion as quickly as possible by washing with a neutral solvent. he solvent adopted was ether, dried as described above. A blank xperiment, carried out by extracting some dried sodium hydrogen lphate (acidity, 40·76 per cent.) with the ether in a Soxhlet pparatus, gave, after prolonged extraction, residues containing)·57 and 40·68 per cent. of sulphuric acid, showing that ether is ithout action on the hydrogen sulphate. Dried sodium hydrogen lphate was shaken continuously in a shaking machine with dried cohol for twenty-four hours, and then filtered off rapidly. The

residue was wrapped in clean paper and extracted in a Soxhlet apparatus with the dried ether until the runnings were neutral. The residue obtained by this method invariably had an acidity lying between 18·66 and 18·74 per cent. of sulphuric acid. Similar results were obtained when the hydrogen sulphate, instead of being shaken with alcohol, was digested with it for several hours under a reflux condenser.

The conclusion is that the action of dry alcohol, either hot or cold, on dry sodium hydrogen sulphate results in the formation of the intermediate sulphate, $Na_2SO_4,NaHSO_4$, containing 18·7 per cent. of acidity as sulphuric acid.

$$3NaHSO_4 = H_2SO_4 + Na_2SO_4,NaHSO_4.$$

Thus, dry alcohol extracts two-thirds of the acidity from sodium hydrogen sulphate, and the statement found in certain standard works (*loc. cit.*) that sodium hydrogen sulphate is decomposed by alcohol with the formation of neutral sulphate, requires revision. Complete extraction of the acid only takes place when the alcohol is contaminated with water.

The actiou of alcohol on potassium hydrogen sulphate was next examined. The "pure" material was fused until no further loss of weight could be detected. The acidity was 36·15 per cent. (calc.: 36·03 per cent.). Several samples were treated with alcohol and extracted with ether, as in the case of the sodium salt, and the acidity in the residue was estimated. In all the samples the acidity lay between 35·59 and 35·84 per cent. It is thus evident that the decomposition of potassium hydrogen sulphate by dry alcohol is negligible. This result is recorded independently by Borntraeger (*Annali Chim. Appl.*, 1919, **12**, 1).

The action of several other aliphatic alcohols on sodium hydrogen sulphate was examined to see if their behaviour is similar to that of ethyl alcohol. The results are given in table II.

TABLE II.

Action of certain Aliphatic Alcohols on Dry Sodium Hydrogen Sulphate.

Alcohol.	Boiling point under 610 mm. pressure.*	Acidity of residue. Per cent.
Methyl alcohol	59·5°	18·68
Ethyl alcohol	72·5°	18·68
n-Butyl alcohol	110–111°	18·65
Amyl alcohol	125·0°	18·66

* Normal pressure at the laboratory at which the work was done.

The Nature of the Reaction between Alcohol and Sodium Hydrogen Sulphate.

During the investigation of the reaction by repeated washings with alcohol on a filter, the washings were collected and the acidity was determined by titration. It was noticed that the acid found in the washings was always less than that which had disappeared from the salt. It was suspected that this discrepancy was due to the formation of ethyl hydrogen sulphate. The liquors were examined for this substance, and its presence was confirmed.

The method of analysis employed for determining in these alcoholic extracts both the total acidity and the extent of conversion into ethyl hydrogen sulphate is that described above under "alcoholic sulphuric acids."

The question then arose: Is the ethyl hydrogen sulphate formed as a result of direct action between the alcohol and the hydrogen sulphate, or is its formation a secondary reaction between the alcohol present and the sulphuric acid extracted directly from the hydrogen sulphate?

The solution of the problem involved an examination of the reaction occurring when dry alcohol and dry sulphuric acid are mixed in varying proportions. The detailed results of this examination will be given in a separate paper, and it is sufficient to state here that:

(1) At the ordinary temperature (18° to 19°) equilibrium between the product, ethyl hydrogen sulphate, and the reacting substances is reached very slowly, and requires about two or three weeks for completion.

(2) The extent of the conversion depends on the proportions in which the reacting substances are present.

The curve indicates the percentage esterification of the total sulphuric acid present for varying proportions of alcohol and sulphuric acid after equilibrium has been attained.

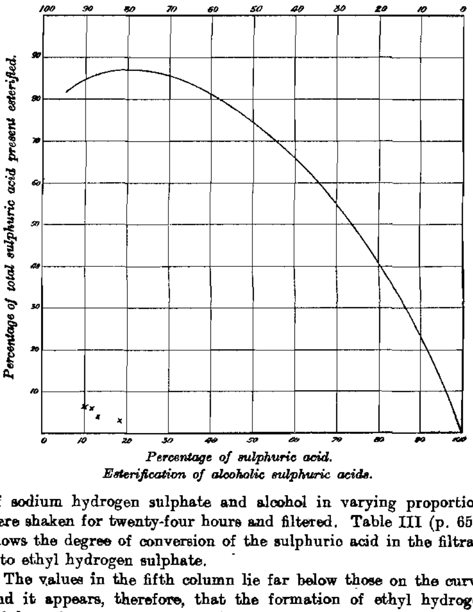
The answer to the question proposed was found by a comparison of results obtained with acid alcoholic liquids prepared from sodium hydrogen sulphate with the values on the above curve.

Since the action represented by the equation

$$H_2SO_4 + EtOH \rightleftharpoons EtHSO_4 + H_2O$$

takes some time to reach equilibrium, it follows that, if the presen of ethyl hydrogen sulphate in the liquor prepared from sodiu hydrogen sulphate is due to this reaction, the examination of suc liquors immediately after the substances have been shaken togeth should show percentage conversion lower than those on the abov curve. If, on the other hand, the ethyl hydrogen sulphate is pr

duced as a result of direct action between the alcohol and the hydrogen sulphate, the value should lie either on its curve or above it, according as the reaction $EtHSO_4 + H_2O \rightarrow EtOH + H_2SO_4$ reaches equilibrium quickly or slowly. (The velocity of this reaction was not studied quantitatively during this work, but it has been observed that the hydrolysis takes place slowly.) Quantities



Esterification of alcoholic sulphuric acids.

of sodium hydrogen sulphate and alcohol in varying proportions were shaken for twenty-four hours and filtered. Table III (p. 657) shows the degree of conversion of the sulphuric acid in the filtrate into ethyl hydrogen sulphate.

The values in the fifth column lie far below those on the curve, and it appears, therefore, that the formation of ethyl hydrogen sulphate is a secondary reaction between alcohol and sulphuric acid, the latter being produced as the result of a primary reaction between alcohol and hydrogen sulphate. It has not been found possible to ascertain the precise nature of this primary reaction.

Experiments were performed in order to ascertain whether the

TABLE III.

Sodium hydrogen sulphate. Grams.	Ethyl alcohol. Grams.	Acidity of filtrate as percentage of sulphuric acid. By direct titration.	Total.	Esterification. Per cent.	Acid extracted. Theory = 2·72 grams. Grams.
10	12	18·12	18·31	2·07	2·69
10	12	18·44	18·73	3·10	2·77
10	18	12·90	13·10	3·05	2·71
10	21	10·99	11·30	5·48	2·68
10	24	9·70	9·98	5·61	2·66
10	24	9·74	10·04	5·97	2·68

process of extraction of the acid is practically instantaneous or whether it takes some time. The results are shown in table IV, from which it will be seen that the extraction is rapid, but not instantaneous. Powdered sodium hydrogen sulphate was vigorously shaken with alcohol for the time shown in the third column. As the time of shaking increased, the mixture became more viscous. The actual time allowed for filtration is shown in the fourth column. The total quantity of acid extracted from the 5 grams of hydrogen sulphate was calculated from the acidity of the filtrate. The tests, although not of a high degree of accuracy, are sufficiently conclusive to give the desired information.

TABLE IV.

Estimation of the Rate of Extraction of Sulphuric Acid from Sodium Hydrogen Sulphate by means of Alcohol.

Sodium hydrogen sulphate. Grams.	Alcohol. Grams.	Time during which the mixture was shaken. Minutes.	Time allowed for filtration. Minutes.	Weight of filtrate. Grams.	Percentage of acid in filtrate. Theory 8·8.	Weight of acid actually recovered. Grams. Theory 1·36.
5	14·1	1·0	0·75	6·097	5·07	0·75
5	14·0	2·0	1·0	2·925	6·97	1·05
5	14·0	4·0	2·0	2·188	8·02	1·22
5	14·0	8·0	3·0	1·981	8·27 8·39	1·24 1·28

The maximum amount of extraction shown in this table amounts to 94·1 per cent. of that theoretically possible. From the last column of table III, it will be seen that when the extraction is continued for twenty-four hours, the acid extracted from the sodium hydrogen sulphate agrees with that demanded by theory, assuming the quantitative conversion of the sodium hydrogen sulphate into the compound $Na_2SO_4,NaHSO_4$. Subsequent investigation showed that extraction for two hours is more than sufficient to ensure the completion of this reaction.

The Action of Alcoholic Sulphuric Acid on Pure, Dry Sodium Sulphate.

Powdered sodium sulphate was mixed with more than twice its weight of alcoholic sulphuric acid, shaken for seventy-two hours, and then filtered off. The acid in the filtrate was determined as in the alcoholic sulphuric acids. The salt was quickly removed from the filter, wrapped in clean paper, and extracted by means of ether in a Soxhlet apparatus until the runnings were neutral. During the shaking, all mixtures become more or less gelatinous. The time during which the extraction lasted is given in the second column of table V. The figure in brackets indicates the number of hours of that time during which the continuous extraction in the Soxhlet apparatus was proceeding. For the rest of the time the substance was lying immersed in the ether. The times only give an approximate idea of the time taken for extraction, as, owing to the difficulty of judging the end-point, it is probable that some samples were left exposed to the action of the ether longer than was absolutely necessary. The two results shown under Nos. 6 and 7 in table V illustrate the considerable length of time required in these cases to complete the reaction.

TABLE V.

Action of Alcoholic Sulphuric Acid on Dry Sodium Sulphate.

No.	Time extracted.	Percentage of acid in the alcoholic sulphuric acid.	Percentage conversion into ethyl hydrogen sulphate of constituents. Acid.	Alcohol.	Acidity in residue as percentage of sulphuric acid.	Notes.
1	6½ days (20)	9·19	82·5	3·9	0·57	
2	—	20·41	87·7	10·6	1·53	
3	8½ days (36)	29·9	83·7	17·5	5·83	
4	9 days (41)	40·6	81·0	26·2	10·83	
5	9 days (41)	50·6	72·5	34·0	12·49	
6	11 days (53)	70·2	54·5	60·4	19·98	incomplete.
	18 days (102)	70·2	54·5	60·4	18·80	neutral washings.
7	15 days (65)	78·8	41·0	71·5	27·69	incomplete
	23 days (117)	78·8	41·0	71·5	18·59	neutral washings.

From these results it will be observed that sodium sulphate combines with sulphuric acid presented to it as alcoholic sulphuric acid. The amount of combination increases with the strength of the alcoholic sulphuric acid used, but is not directly proportional to it. The table gives the results after the sodium sulphate had

been left in contact with the alcoholic sulphuric acid for seventy-two hours with constant shaking. Owing to pressure of work, it was not possible to examine the influence of time on the action of alcoholic sulphuric acids on sodium sulphate.*

The Action of Alcoholic Sulphuric Acid on Dry Sodium Hydrogen Sulphate.

Sodium hydrogen sulphate was mixed with about six times its weight of alcoholic sulphuric acid and shaken for twenty-four hours. The solid was then filtered off, wrapped in clean paper, and placed in a Soxhlet apparatus for extraction with dry ether. The acidity of the residue in the paper was estimated as soon as the runnings from the apparatus were neutral. The observed results are given in table VI.

TABLE VI.

Action of Alcoholic Sulphuric Acid on Dry Sodium Hydrogen Sulphate.

No.	No. of hours extracted.	Strength of alcoholic sulphuric acid as percentage of sulphuric acid.	Percentage conversion of constituents into ethyl hydrogen sulphate.		*As percentage of sulphuric acid.*	
			Acid.	Alcohol.	Acidity in filtrate after shaking.	Acidity of residue
1	13	9·1	82·5	3·9	13·5	18·83
2	34	21·6	87·1	11·3	28·8	18·64
3	38	29·9	83·7	17·5	32·9	26·31
4	82	40·6	81·0	26·2	39·1	27·69
5	38	50·6	72·5	34·0	50·1	23·62
	?	50·6	72·5	34·0	50·1	18·93
6	34	60·6	64·5	44·5	57·5	33·60
	74	60·6	64·5	44·5	57·5	18·63
7	50	70·2	54·5	60·4	67·8	27·86
8	86	78·8	41·0	71·5	78·1	23·63

* It is necessary to exercise great care in testing the runnings with litmus paper as, when the acid is small in quantity, its presence is not indicated until all the ether has evaporated from the paper.

In the cases of specimens treated with alcoholic sulphuric acids of the higher acid-contents, it was observed that the liquor in the flask of the Soxhlet apparatus separated into two layers. This was due to the presence of ethyl hydrogen sulphate. This substance was also found in washings in which no separation into layers had occurred. The solubility of ethyl hydrogen sulphate in ether is less than one per cent., and consequently, if there is much ethyl hydrogen sulphate present, it shows itself by causing the appearance of two layers in the flask.

These remarks apply also to the next section.

From these figures it is evident that alcoholic sulphuric acid reacts with sodium hydrogen sulphate. It appears that alcoholic sulphuric acids of which the strength is about 20 per cent. and less extract acid from the hydrogen sulphate and leave a residue of the compound $Na_2SO_4,NaHSO_4$, whilst acids of 30 per cent. and more also react with the hydrogen sulphate and give another sulphate of sodium, which has previously been prepared by a different method, having the formula $Na_2SO_4,2NaHSO_4$ and an acidity of 25·65 per cent. The formation of this compound has not been definitely proved, but, if it is formed, it is decomposed by exhaustive extraction with ether, giving the compound

$$Na_2SO_4,NaHSO_4.$$

The mixtures of alcoholic sulphuric acid and sodium hydrogen sulphate become gelatinous during the shaking, and, if the substance in the Soxhlet apparatus is examined during the extraction, crystals of considerable size are found. These crystals seem to be formed in the bottle or during the extraction, for the hydrogen sulphate was always carefully powdered before exposing it to the action of the alcoholic sulphuric acid. The crystals probably consist of the compound $Na_2SO_4,2NaHSO_4$, as they are not observed when the product of the extraction is the compound

$$Na_2SO_4,NaHSO_4.$$

The extraction was fairly rapid at first, and the litmus with which the runnings were tested showed a bright pink coloration. After some time the extraction became very slow, and the acidity towards litmus paper was obvious, but extremely weak (see footnote, p. 659). This will explain the various times shown in the table for extraction; for example, one sample, after actual extraction for eighty-two hours and remaining in ether for the remainder of a fortnight when the extraction was not proceeding, showed an acidity of 27·7 per cent. The remainder of the sample was then replaced and was extracted for twenty-four hours more, and when not under continuous extraction was left in the dry ether, the whole experiment lasting about three days. After this treatment the acidity was 24·7 per cent. As a comparison, it may be stated that the ethereal extraction of sodium hydrogen sulphate, after treatment with alcohol, takes only a few hours to complete.

It will be observed that the acidity of the filtrates in cases 1, 2, and 3 is greater than the original acidity of the alcoholic sulphuric acid; in all other cases it is about the same or a little less.

Discussion of certain Properties of the Intermediate Sulphate, $Na_2SO_4,NaHSO_4$.

The compound, $Na_2SO_4,NaHSO_4$, which is so readily formed by the action of dry alcohol on dry sodium hydrogen sulphate, is dealt with by Pascal and Ero (*loc. cit.*), although the substance was prepared by a different method from that described in this paper. In the course of the present work it has been necessary to study this compound in some detail, and the results do not confirm the observations of Pascal and Ero, who state that the intermediate sulphate decomposes at 174° with partial liquefaction. Specimens of the intermediate sulphate, $Na_2SO_4,NaHSO_4$, were prepared by extraction of sodium sulphate by alcohol, and the statement that the substance is unchanged in air was confirmed. The acidity of the different samples ranged from 18·66 to 18·78 per cent. A weighed quantity of the substance was then heated in a platinum basin in an oil-oven, and cooled and weighed at intervals. The temperature of the bath was raised about 4° or 5° at a time until the temperature reached 215°. The salt was kept in the bath for about half an hour at each temperature, and weighed after each heating. It showed no signs of melting, and its weight was constant. Over the whole period of a particular experiment, *7·3038 grams of the substance lost 0·0254 gram. The acidity at* the commencement of the experiment was 18·67 per cent., and the acidity after the prolonged heating was 18·74 per cent. This result has been frequently confirmed. The only difference in the substance after heating was that the colour had changed to a pale grey. The salt as prepared is snow-white. Every attempt on the part of the authors to determine the melting point resulted in failure. Even when heated to 260° the substance did not melt. It seemed possible that Pascal and Ero, having prepared their specimens from solutions, might have determined the melting point of a substance containing water, and that the presence of water would cause it to melt. A sample of the intermediate sulphate was prepared by the recrystallisation of nitre-cake (33 per cent. of sulphuric acid), and gave the following analysis:

	I. Found. Per cent.	II. Calculated from I, assuming the salt dehydrated.	III. Theory for the dry salt.
Acidity as H_2SO_4	18·45, 18·50	19·28	18·70
SO_4 determined as $BaSO_4$	70·58	73·41	73·29
Na_2SO_4 produced on fusion	77·42, 77·43	80·69	81·30
Water	3·95, 4·02	—	—

The salt obtained by recrystallisation contained a slight excess of acid above that required for the intermediate compound. On heating, water was given off, but fusion did not take place. The authors are unable to account for the observations quoted in the paper mentioned (*loc. cit.*). The substance, $Na_2SO_4,NaHSO_4$, decomposes before it melts, the residue after heating being fused sodium sulphate.

The Action of Pure, Dry Alcohol on Mixtures of Pure, Dry Sodium Sulphate and Pure, Dry Sodium Hydrogen Sulphate before and after Heating the Mixtures.

The next series of experiments was carried out with the object of elucidating the composition of commercial nitre-cake. It is usually assumed that nitre-cake is a mixture of sodium hydrogen sulphate and sodium sulphate, but recently Pascal and Ero (*loc. cit.*) have stated that, at the ordinary temperature, it is a mixture of the intermediate sulphate, $Na_2SO_4,NaHSO_4$, and the hydrogen sulphate. Pascal and Ero's statement is based on a study of the melting points of mixtures of neutral sulphate and sulphuric acid, and their conclusions are not therefore necessarily applicable to nitre-cake. It occurred to the authors that a study of the action of alcohol on (1) mixtures of sodium sulphate and hydrogen sulphate, and (2) commercial nitre-cake, would probably throw light on the subject, and experiments were accordingly carried out on these lines. As a preliminary experiment, it was necessary to ascertain if there is any evolution of sulphuric acid from such mixtures when heated to 215°, as the conclusions drawn depend on the assumption that, before extraction with alcohol, the total amount of acid in the mixture is the same as the amount of acidity in the mixture when weighed out for the experiment. Results show that mixtures of sodium sulphate and sodium hydrogen sulphate do not lose sulphuric acid when heated to 215°.

(*a*) *Table VII. Nos.* 1 *to* 7.—Dry sodium sulphate and dry sodium hydrogen sulphate were shaken with excess of alcohol for twenty-four hours. The solid was then filtered off and extracted with dry ether until the runnings were neutral.

(*b*) *Table VII. Nos.* 8 *to* 13.—In all these cases the salts were treated as above, except that, before the alcohol extraction, the mixed salts were heated *in an oil-oven for four hours at 200—215°*. In No. 13 the mixture was heated for six and a-half hours to see if the reaction became quantitative if given sufficient time. The analyses indicate that the reaction was complete in the shorter time, namely, *four hours.*

The values shown in column vii are found by calculation, assuming *that all the sodium hydrogen sulphate is converted into the* compound, Na_2SO_4,$NaHSO_4$, and that as much sodium sulphate as possible combines with the sulphuric acid so liberated, also forming the compound, Na_2SO_4,$NaHSO_4$.

It will be seen that, in every case, the acidity of the residue is greater than it would be if the hydrogen sulphate only took part in the reaction (column iv), but less than the value shown in column vii. Participation of the sodium sulphate in the reaction is indicated in every case, although (see column viii) its conversion into the compound, Na_2SO_4,$NaHSO_4$, is never complete.

Two explanations are possible of the part taken by the sodium sulphate in the reaction:

(1) That, in the presence of alcohol, some of the sulphate combines directly with the sodium hydrogen sulphate. No evidence in favour of this possibility has been found.

(2) That the alcoholic sulphuric acid produced by the action of the alcohol on the sodium hydrogen sulphate reacts with a portion of the sulphate, forming the compound, Na_2SO_4,$NaHSO_4$.

Sulphuric acid acts on sodium sulphate in the presence of water, and it seemed not unlikely that it might act on sodium sulphate *in the presence of alcohol. This point was thoroughly investigated*, and the results obtained (p. 658) show conclusively that (*a*) anhydrous sodium sulphate is acted on by alcoholic sulphuric acid at the ordinary temperature, and (*b*) that the amount of interaction increases with the strength of alcoholic sulphuric acid employed.

In the second series of analyses, obtained in experiments in which the substances under consideration were heated, it will be seen that the heating of the two salts in contact results in a very considerable formation of the compound, Na_2SO_4,$NaHSO_4$, as indicated by the increased acidity of the residue after extraction (see table VII, columns v to viii, and compare Nos. 8 to 13 with Nos. 1 to 7). The mixtures (except No. 13) were heated for four hours at 200—215°. Prolonged heating does not increase the yield of intermediate sulphate. Considering the difficulties of complete admixture and the fact that the mixtures never completely fused, the results lead one to expect a still higher conversion to the compound under ideal conditions. It appears that if the ratio $Na_2SO_4 : NaHSO_4$ is greater than unity, the degree of conversion to the double compound is greater than when the ratio $NaHSO_4 : Na_2SO_4$ is greater than unity.

TABLE VII.

Action of Pure, Dry Alcohol on Mixtures of Sodium Sulphate and Sodium Hydrogen Sulphate both before and after Heating.

Mixtures of sodium sulphate and sodium hydrogen sulphate not heated after mixing.

Expt. No.	Composition of mixture.		Corresponding with approximate molecular proportions.	Initial acidity of mixture. Per cent. H_2SO_4.	Acidity of residue. Per cent. H_2SO_4.	Calculated acidity of residue assuming complete conversion of $NaHSO_4$ into $Na_3H(SO_4)_2$, the Na_2SO_4 remaining unaffected. Per cent. H_2SO_4.	Calculated acidity of residue assuming maximum possible conversion of both $NaHSO_4$ and Na_2SO_4 into the compound $Na_3H(SO_4)_2$. Per cent. H_2SO_4.	Conversion of Na_2SO_4 into $Na_3H(SO_4)_2$ expressed as the percentage of the total Na_2SO_4 originally present which could have been so converted.
	Na_2SO_4. Per cent.	$NaHSO_4$. Per cent.						
1	70·3	29·7	$2Na_2SO_4 : NaHSO_4$ ...	12·1	7·74	4·40	12·1	43·4
2	54·2	45·8	$Na_2SO_4 : NaHSO_4$ ...	18·7	9·88	7·08	18·7	23·9
3	37·2	62·8	$Na_2SO_4 : 2NaHSO_4$ ...	25·6	13·20	10·31	18·7	34·5
4	20·0	80·0	$Na_2SO_4 : 4{\cdot}7NaHSO_4$	32·6	17·31	13·92	18·7	71·0
5	17·0	83·0	Composition of nitre-cake if it were a mixture of Na_2SO_4 and $NaHSO_4$.	33·8	15·98	14·59	18·7	33·6
6	8·6	91·4	Approximately $Na_2SO_4 : 13NaHSO_4$.	37·3	17·16	16·57	18·7	26·6
7	0·0	100·0	$NaHSO_4$	40·8	18·69	18·70	18·7	—

	Mixtures of sodium sulphate and sodium hydrogen sulphate heated at 200—215° after pulverisation and intimate mixing.							
8	70·3	29·7	$2Na_2SO_4 : NaHSO_4$ ...	12·1	11·50	4·40	12·1	92·2
9	64·8	35·2	$3Na_2SO_4 : 2NaHSO_4$ ...	14·4	14·85	5·30	15·2	96·3
10	54·2	45·8	$Na_2SO_4 : NaHSO_4$ ...	18·7	15·71	7·08	18·7	74·2
11	37·2	62·8	$Na_2SO_4 : 2NaHSO_4$ ...	25·6	17·01	10·31	18·7	80·6
12	29·7	70·3	$Na_2SO_4 : 3NaHSO_4$ ...	28·7	17·29	11·84	18·7	79·5
13	37·2	62·8	$Na_2SO_4 : 2NaHSO_4$ ...	25·6	16·94	10·31	18·7	79·0 Mixture heated 6½ hours.
	Substances prepared from sodium nitrate and sulphuric acid, that is, nitre-cakes.							
14	17·0	83·0	Nitre-cake from factory retort.	33·8	18·78	14·59	18·7	100·0
15	54·2	45·8	Nitre-cake prepared in laboratory to give molecular proportions. $Na_2SO_4 : NaHSO_4$.	19·0	18·58	7·08	18·7	99·0
16	70·6	29·4	Nitre-cake prepared in laboratory.	12·0	11·96	4·35	12·00	—
Col.	i.	ii.	iii.	iv.	v.	vi.	vii.	viii.

Constitution of Nitre-cake.

The results given in table VII provide conclusive evidence regarding the constitution of nitre-cake. It will be noticed from experiments Nos. 14, 15, and 16 that:

(*a*) When the original acidity of the cake is more than 18·7 per cent., extraction with dry alcohol reduces it to 18·7 per cent., indicating a complete conversion of the sodium hydrogen sulphate present in the cake into the compound, $Na_2SO_4,NaHSO_4$.

(*b*) When the original acidity of the cake is about 18·7 per cent., treatment with dry alcohol leaves it unaltered.

(*c*) When the original acidity of the cake is less than 18·7 per cent., treatment with dry alcohol again leaves it unaltered.

Experiments 1 to 6 having shown that when mixtures of sodium sulphate and sodium hydrogen sulphate are extracted with alcohol the sodium sulphate is never completely converted into the compound, $Na_2SO_4,NaHSO_4$, it follows from the above results that nitre-cakes of 18·7 per cent. acidity and more contain no sodium sulphate at all. Cakes of more than 18·7 per cent. acidity consist of a mixture of sodium hydrogen sulphate and the compound, $Na_2SO_4,NaHSO_4$, and cakes of less than 18·7 per cent. acidity comprise a mixture of sodium sulphate and the compound,

$$Na_2SO_4,NaHSO_4,$$

containing no hydrogen sulphate at all, for, if hydrogen sulphate were present, extraction with alcohol would reduce the acidity. Finally, a cake of 18·7 per cent. acidity consists of the compound, $Na_2SO_4,NaHSO_4$, and contains neither sulphate nor hydrogen sulphate.

The molecular proportions of a nitre-cake of known acidity may be calculated from one of the two formulæ given below:

(*a*) If the acidity of the nitre-cake is 18·7 per cent. sulphuric acid or less, $x = 1 - \frac{142y}{4900 - 120y}$, where x = the molecular proportion of sodium sulphate, $(1-x)$ = the molecular proportion of the compound, $Na_2SO_4,NaHSO_4$, in the cake, and y = its acidity as percentage of sulphuric acid.

(*b*) If the acidity is 18·7 per cent. of sulphuric acid, or more, but not exceeding 40·83 per cent., $x = \frac{4900 - 120y}{142y}$, where x = the molecular proportion of the compound, $Na_2SO_4,NaHSO_4$, $(1-x)$ = the molecular proportion of sodium hydrogen sulphate in the nitre-cake, and y = its acidity as percentage of sulphuric acid.

Summary and Conclusions.

(1) Dry alcohol acts on dry sodium hydrogen sulphate, with the formation of the intermediate sulphate, $Na_2SO_4,NaHSO_4$, and the liberation of sulphuric acid, which dissolves in the alcohol, and is subsequently converted partly into ethyl hydrogen sulphate. Prolonged action of alcohol does not extract any further quantity of the acid.

(2) Methyl, *n*-butyl, and amyl alcohols also react with sodium hydrogen sulphate, with the formation of the same intermediate sulphate.

(3) Dry ethyl alcohol does not decompose dry potassium hydrogen sulphate.

(4) Moist alcohol will completely decompose sodium hydrogen sulphate, giving first the intermediate sulphate, $Na_2SO_4,NaHSO_4$, and finally normal sodium sulphate. Sodium sulphate is sparingly soluble in moist alcohol.

(5) Alcoholic sulphuric acid reacts with sodium sulphate in the cold (18°), with the formation of an acid sulphate. The amount of the interaction increases with the strength of the alcoholic sulphuric acid employed.

(6) When alcoholic sulphuric acid acts on sodium hydrogen sulphate, the intermediate sulphate, $Na_2SO_4,NaHSO_4$, is formed if the strength of the alcoholic sulphuric acid corresponds with 20 per cent. or less. When the alcoholic sulphuric acid has a strength corresponding with 30 per cent. of sulphuric acid or more, the compound, $Na_2SO_4,2NaHSO_4$, is probably produced; if so, this compound is slowly decomposed by constant extraction with pure, dry ether, and finally yields the compound, $Na_2SO_4,NaHSO_4$.

(7) The compound, $Na_2SO_4,NaHSO_4$, is formed when dry sodium sulphate is heated with dry sodium hydrogen sulphate.

(8) Nitre-cake consists of the compound $Na_2SO_4,NaHSO_4$, alone or mixed with either sodium hydrogen sulphate or sodium sulphate, according as the acidity is equal to, greater than, or less than 18·7 per cent. of sulphuric acid.

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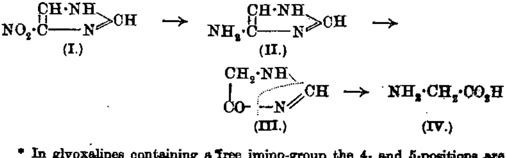
LXX.—*Orientation of the Nitro- and Arylazo-glyoxalines. Fission of the Glyoxalone Nucleus.*

By Robert George Fargher.

In the course of a recent communication (T., 1919, **115**, 217), the author, in conjunction with Prof. F. L. Pyman, showed that the nitro-group, on entering the glyoxaline nucleus, takes up the 4- or 5-position.* Subsequent reduction with tin and hydrochloric acid, undertaken with the object of examining the corresponding amino-glyoxalines and determining directly the orientation of the nitro-group, led to fission of the nucleus, two of the three nitrogen atoms appearing in the form of ammonia. It was suggested that the first stage of the disintegration was probably the elimination of the amino-group as ammonia with formation of a glyoxalone, certain members of the purine group—also derivatives of 4-amino-glyoxaline—having been shown to undergo hydrolysis in this manner (compare Tafel and Meyer, *Ber.*, 1908, **41**, 2546; Biltz, *Ber.*, 1910, **43**, 1589). It was therefore of interest to investigate the reduction in more detail with the objects (1) of determining directly the orientation of the nitro-group, (2) of establishing the transformation into the glyoxalone, and (3) of studying the fission of the simple glyoxalone nucleus under the influence of acids. The earlier experiments had shown that the products of complete reduction, apart from ammonium chloride, the predominant constituent, were very uninviting in appearance. Consequently, treatment in cold hydrochloric acid solution with just sufficient stannous chloride to reduce the nitro-group was employed, with success. Nitro-glyoxaline, in addition to ammonia, yielded glycine, as did also nitro-2-methylglyoxaline, whilst nitro-5-methylglyoxaline yielded α-alanine. This clearly demonstrates that the nitroglyoxalines are correctly formulated as 4-nitro-derivatives, that the reduction is followed by hydrolysis of the 4-aminoglyoxaline (II), with the



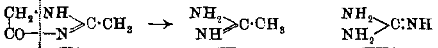
* In glyoxalines containing a free imino-group the 4- and 5-positions are equivalent.

formation of the 4-glyoxalone (III), and that one fission of the 4-glyoxalone nucleus takes place between the 1:2- and 3:4-positions. This fission recalls the isolation of sarcosine,

$$NHMe\cdot CH_2\cdot CO_2H,$$

by *Rosengarten and Strecker* (*Annalen*, 1871, **157**, 1) as a *product* of hydrolysis of caffeine by baryta.

The reduction of nitro-2-methylglyoxaline gave evidence of a second mode of fission, as *α*-amino-*α*-iminoethane (VI) was isolated.

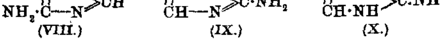


(V.) (VI.) (VII.)

Fission therefore takes place between the 1:5- and 3:4-positions (V), *presumably with simultaneous formation of glycollic acid*, and reveals the probable mechanism of the formation of guanidine (VII) in the reduction of 2-benzeneazoglyoxaline.

What is practically the reverse process was accomplished by Finger (*J. pr. Chem.*, 1907, [ii], **76**, 93), who condensed *α*-imino-*α*-ethoxyethane with the ethyl ester of glycine, and obtained 2-methyl-4-glyoxalone.

In neither of these reductions was the aminoglyoxaline obtained. Consequently, the isolation of a small and variable proportion of 4-*amino-5-methylglyoxaline* (VIII) from the reduction of 4-nitro-5-methylglyoxaline was both unexpected and important, and permitted comparison of a simple 4-aminoglyoxaline with the 2-aminoglyoxaline isolated in the earlier work (*loc. cit.*, pp. 223, 246). It was already evident that they evinced a considerable difference in stability, and *the dissimilarity extends to most of the other properties*. Whilst 2-aminoglyoxaline (IX) is a monacidic base, which does not yield a benzylidene derivative, does not react with sodium-*β*-naphthoxide after treatment with nitrous acid,* and, in brief, behaves in many of its reactions as if it existed in the tautomeric form (X), 4-amino-5-methylglyoxaline reacts as a true aromatic amine, forming a *dihydrochloride* and a crystalline *benzylidene* derivative, and coupling readily with sodium-*β*-naphthoxide after treatment with nitrous acid.



(VIII.) (IX.) (X.)

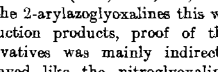
In the previous communication it was also shown that the arylazoglyoxalines were true *C*-azo-, and not *N*-azo-, compounds, as had

* I am indebted to Prof. Pyman, who has, since the appearance of our joint communication, made a further study of the 2-aminoglyoxalines, for this correction (compare *loc. cit.*, p. 248).

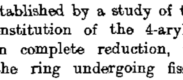
been suggested by Rung and Behrend (*Annalen*, 1892, **271**, 28) and Burian (*Ber.*, 1904, **37**, 696). Whilst, however, in the case of the 2-arylazoglyoxalines this was established by a study of their reduction products, proof of the constitution of the 4-arylazo-derivatives was mainly indirect. On complete reduction, they behaved like the nitroglyoxalines, the ring undergoing fission, whilst their general properties were antagonistic to the supposition that they were 1-arylazo-derivatives.

As the results now obtained with the nitroglyoxalines indicated the course the reaction might be expected to take, it was evident that the formation of glyoxalone derivatives in the reduction of the 4-arylazoglyoxalines would definitely determine the orientation of the arylazo-group.

The reduction of *p*-bromobenzeneazo-2-methylglyoxaline and 4-benzeneazo-5-methylglyoxaline was therefore undertaken under the same conditions as had been successful in the case of the nitroglyoxalines. The former, which, previously, had yielded only *p*-bromoaniline and ammonia as isolable reduction products, readily gave a *glyoxalone*, for which there were two possible formulæ (XI, XII).

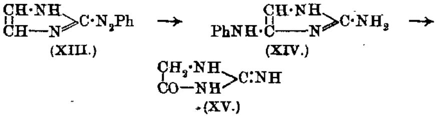


(XI.)



(XII.)

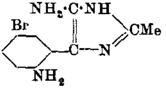
The formation of a *benzylidene* derivative similar to that obtained from 2-amino-4-*p*-aminophenylglyoxaline shows the second of these to be correct. The failure, therefore, of the compound to give more than a faint yellow colour with sodium-β-naphthoxide after treatment with nitrous acid is interesting. The comparative stability towards hydrochloric acid serves to confirm the constitution, as an earlier stage in the formation of glycocyamidine (XV) and alacreatinine from 2-benzeneazoglyoxaline (XIII) and 2-benzeneazo-5-methylglyoxaline respectively, by reduction with zinc and acetic acid, is no doubt represented by 2-amino-4-anilinoglyoxaline (XIV) and 2-amino-4-anilino-5-methylglyoxaline, which then undergo hydrolysis and rearrangement.

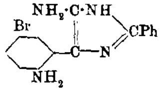


(XIII.) (XIV.) (XV.)

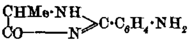
Practically the whole of the reduction product appeared in the

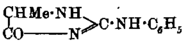
form of an insoluble stannichloride, probably that of 5-*amino*-4-(2′-*amino*-5′-*bromophenyl*)-2-*methylglyoxaline* (XVI), as, after


(XVI.)


(XVII.)

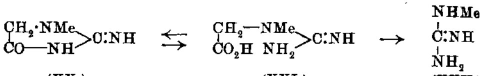
conversion into the hydrochloride, roughly molecular proportions of ammonium chloride and the glyoxalone were obtained on fractionation. It is therefore permissible to assume that the constitution of the reduction product of bromobenzeneazo-2-phenylglyoxaline (*loc. cit.*, p. 258) is correctly represented as 5-*amino*-4-(2′-*amino*-5′-*bromophenyl*)-2-*phenylglyoxaline* (XVII), the product evincing a greater stability towards acids than the corresponding 2-methyl derivative. The further study of the reduction of 4-benzeneazo-5-methylglyoxaline was of interest, as two products of undetermined constitution had already been isolated, a base $C_9H_{10}ON_2$, from the reduction with tin and hydrochloric acid (*loc. cit.*, p. 254), and a base, $C_{10}H_{11}ON_3$, from the reduction with zinc and acetic acid (*loc. cit.*, p. 255). The reduction with cold stannous chloride has now yielded, in addition to the base, $C_9H_{10}ON_2$, a third compound, $C_{10}H_{11}ON_3$, not identical with the product of the zinc reduction. It gave a *dihydrochloride*, a *benzylidene* derivative, and, after treatment with nitrous acid, coupled with sodium-β-naphthoxide, and is therefore 2-*p*-*aminophenyl*-5-*methyl*-4-*glyoxalone* (XVIII).


(XVIII.)


(XIX.)

The base from the zinc reduction was monacidic, did not couple, and did not react with benzaldehyde, and is therefore 2-*anilino*-5-*methyl*-4-*glyoxalone* (XIX). It is of interest to record that the reactions which have been examined so far indicate that the zinc and acetic acid reduction favours the semidine change, whilst the stannous chloride reduction favours the benzidine change. It does not follow, however, that the reaction proceeds entirely in the one direction, as, for example, a small proportion of 2-5′-bromo-2′-aminoanilinoglyoxaline (*loc. cit.*, p. 246) is produced in the reduction of 2-*p*-bromobenzeneazoglyoxaline, whilst the guanidine formed in the reduction of 2-benzeneazoglyoxaline conceivably originates from 2-amino-4-anilinoglyoxaline through the intermediate formation of glycocyamidine. This is of interest in view of the close

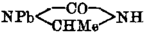
relationship of creatine (XXI) to creatinine (XX) and the suggestion that the former is the precursor of methylguanidine (XXII)



(XX.) (XXI.) (XXII.)

in the organism (Achelis, *Zeitsch. physiol. Chem.*, 1906, **50**, 10).

Neither of the modes of fission established in the simple glyoxalone nucleus accounts for the formation of the base, $C_9H_{10}ON_2$, from either 2-*p*-aminophenyl-5-methyl-4-glyoxalone or 2-anilino-5-methyl-4-glyoxalone, one of which probably represents an earlier stage in its formation. It is difficult to avoid the supposition that fission ensues between the 4:5- and 2:3-positions, the reaction being conditioned by the presence of the *p*-aminophenyl or anilino-grouping in the 2-position. The small amount of these substances available has rendered it impossible, so far, to examine their hydrolytic products in detail, but it is worth noting that in the former case the properties of the base necessitate the assumption of subsequent ring-formation involving the *p*-amino-group, whilst, in the latter, a cyclic derivative of carbamide (XXIII) is one of the possible products.



(XXIII.)

$$NHPh{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}NHPh$$

(XXIV.)

Attempts to synthesise this by the condensation of acetal or acetaldehyde with phenylcarbamide led, however, solely to *ethylidenebisphenylcarbamide* (XXIV).

Experimental.

Reduction of 4-Nitroglyoxaline. Formation of Glycine and Ammonia.

To 33 grams of nitroglyoxaline, dissolved in 100 c.c. of concentrated hydrochloric acid, 175 c.c. of stannous chloride solution* were gradually added, the temperature being maintained below 5° and the mixture stirred mechanically for some time after the addition was complete. The crystalline stannichloride was collected, and the filtrate concentrated, when it deposited a further quantity, the total yield being about 49 grams.

On recrystallisation from 10 per cent. hydrochloric acid, it was

* The stannous chloride solution used throughout the investigation was prepared by mixing 40 grams of stannous chloride with sufficient hydrochloric acid to form 100 c.c. of solution.

obtained in large, octahedral masses, which, after removal of tin, gave solely *ammonium chloride* (Found: Cl=66·1; NH_3=31·6. Calc.: Cl=66·3; NH_3=31·8; in the stannichloride, NH_3=9·1, 9·2. Calc.: NH_3=9·3 per cent.). The residual liquor was evaporated to remove excess of acid, freed from tin, again evaporated under diminished pressure, and extracted with alcohol, which left undissolved 6·3 grams of ammonium chloride. The syrupy alcoholic extract, on solution in water and addition of picric acid, yielded only traces of an insoluble picrate, 60 grams of nitroglyoxaline giving 0·5 gram in a pure condition. This separated from water in well-defined needles, which darkened rapidly above 200° and melted at 234° (corr.), and gave analytical figures in fair agreement with *aminoglyoxaline dipicrate*, but the amount was too small to permit of its further examination (Found: C=32·8; H=2·6; N=22·8. $C_3H_5N_3,2C_6H_3O_7N_3$ (541·2) requires C=33·3; H=2·1; N=23·3 per cent.). The residual solution was reconverted into the hydrochloride, evaporated to dryness in a vacuum, dissolved in alcohol, and submitted to fractionation. There first deposited a further 1·0 gram of ammonium chloride, then (*a*) 5·2 grams melting at about 174°, (*b*) 3·1 grams melting at about 156°, and (*c*) 2·8 grams melting between 130° and 140°. Further crops were obtained more readily from the mother liquor after the addition of alcoholic hydrogen chloride, and these melted between 130° and 140°. Crops (*a*) and (*b*) were united and crystallised from rather less than their own weight of water, when, on keeping, there separated 4 grams of large, flattened prisms melting at 189° (corr.), sintering some degrees earlier. This substance proved to be the sesquihydrochloride of glycine (Found: C=25·5; H=6·1; N=14·9; Cl=19·1. $(C_2H_5O_2N)_2,HCl$ requires C=25·7; H=5·9; N=15·0; Cl=19·0 per cent.). The mother liquor, on further concentration, deposited a mixture of this hydrochloride and the normal hydrochloride of glycine, from which the latter was obtained on crystallisation in presence of excess of hydrochloric acid. It separated as a serrated mass of somewhat hygroscopic, flattened prisms, which melted at 182° (corr.), sintering above 150° (Found: C=21·7; H=5·7; N=12·7; Cl=31·2. $C_2H_5O_2N,HCl$ requires C=21·5; H=5·4; N=12·6; Cl=31·8 per cent.). Crop (*c*), and subsequent crops melting at about the same temperature, were mixed and recrystallised from alcohol, when a mass of fine, silky needles, melting at 145° (corr.) and showing no depression when mixed with a synthetic specimen of glycine ethyl ester hydrochloride, was obtained (Found: C=34·5; H=7·4; N=10·0; Cl=25·0. $C_4H_9O_2N,HCl$ requires C=34·4; H=7·2; N=10·0; Cl=25·4 per cent.).

The identity was further established by the isolation of glycine from all three hydrochlorides, the glycine melting at 247° (corr.) and showing no depression of melting point when mixed with a synthetic specimen (Found: C=31·8; H=6·9; N=18·5. $C_2H_5O_2N$ requires C=32·0; H=6·7; N=18·7 per cent.).

The ultimate alcoholic residues, which were very dark in colour, gave no further crystalline material.

Reduction of 4-Nitro-2-methylglyoxaline. Formation of Glycine, α-Amino-α-iminoethane, and Ammonia.

The reduction of 12·7 grams of nitro-2-methylglyoxaline was carried out as in the previous instance. There were first obtained 7·6 grams of ammonium stannichloride. The more soluble stannichlorides were converted into hydrochlorides in the customary manner, the solution evaporated to dryness under diminished pressure, and extracted with alcohol, leaving 3·5 grams of practically pure ammonium chloride. The alcoholic extract was concentrated to a syrup, dissolved in 50 c.c. of water, and treated with a boiling solution of 13 grams of picric acid in 250 c.c. of water, when 7·7 grams of a crude picrate were obtained. This, on recrystallisation from water, separated in glistening, orange prisms sintering from 245° and melting at 252° (corr.). The yield amounted to 3·6 grams. 2·8 Grams of this picrate were converted into the hydrochloride, excess of hydrochloric acid being avoided. The resulting aqueous solution was evaporated to dryness under diminished pressure, below 50°, leaving a solid residue, which was dissolved in a little alcohol and kept. There gradually separated long, colourless, prismatic needles, which melted at 174° (corr.), and proved to be the hydrochloride of α-amino-α-iminoethane (VI, p. 669). Pinner (*Ber.*, 1884, **17**, 178; "Die Iminoäther," p. 107) gives the melting point as 165° or 166—167° (Found: C=25·7; H=7·5; N=29·1; Cl=36·5. $C_2H_6N_2,HCl$ requires C=25·4; H=7·5; N=29·6; Cl=37·5 per cent.).

The melting point of the picrate is given by Dieckmann (*Ber.*, 1892, **25**, 547) as 247° (Found: C=33·8; H=3·3; N=23·9. $C_2H_6N_2,C_6H_3O_7N_3$ requires C=33·4; H=3·2; N=24·4 per cent.).

The identity of the base was further established by the preparation of the *aurichloride*. This salt crystallises from water in fern-shaped clusters of golden-yellow needles, which melt at 266° and are anhydrous.

Found: Au=49·2.

$C_2H_6N_2,HCl,AuCl_3$ (398·1) requires Au=49·5 per cent.

The platinichloride, previously described by Pinner, separates

from water in small, orange, flattened prisms or in large, red, flattened prisms, according to the rate of crystallisation. Like the aurichloride, it is anhydrous. It melts at 242° (corr.) (Found: Pt = 37·0. $(C_2H_6N_2)_2$,2HCl,$PtCl_4$ requires Pt = 37·1 per cent.).

The residual liquor from the separation of the α-amino-α-iminoethane picrate was regenerated into the hydrochloride and evaporated to dryness, leaving a dark syrup. As this showed no tendency to crystallise, it was dissolved in absolute alcohol containing hydrogen chloride, warmed for a short time on the water-bath, and concentrated, when, on keeping, glycine ethyl ester hydrochloride gradually separated, and was identified by comparison with the synthetic product and by analysis (Found: N = 10·0; Cl = 25·1. $C_4H_9O_2N$,HCl requires N = 10·0; Cl = 25·4 per cent.).

The residue from the glycine ester hydrochloride yielded no further crystalline material. A small quantity of a non-nitrogenous ester was isolated, but the amount was too small to attempt its purification and identification.

Reduction of Nitro-5-methylglyoxaline. Formation of α-Alanine, 4-Amino-5-methylglyoxaline, and Ammonia.

The reduction of 11 grams of 4-nitro-5-methylglyoxaline was carried out as in the previous instances, yielding 7·5 grams of ammonium stannichloride and 1·4 grams of ammonium chloride. The syrupy, alcoholic extract was dissolved in 25 c.c. of water and treated with a boiling solution of 8 grams of picric acid in 200 c.c. of water, when there quickly separated 4 grams of fine needles contaminated with oily matter. On keeping overnight, a further 2 grams separated, mainly picric acid, and the mother liqnor deposited picric acid only on concentration. The two crops were crystallised from alcohol, from which there separated clusters of long, old-gold needles, which blackened rapidly above 180° and melted and decomposed at 195° (corr.).

The picrate was converted into the hydrochloride, excess of acid being avoided. The solution, on evaporation in a vacuum at as low a temperature as possible, left a syrup, which became crystalline on mixing with a few drops of alcohol. The *hydrochloride* separates from alcohol in minute, colourless prisms, which melt at 189° (corr.) and are anhydrous. The crystallisation should be conducted as quickly as possible, as the alcoholic solution decomposes on keeping.

Found: C = 28·2; H = 5·6; N = 24·2; Cl = 41·0.

$C_4H_7N_3$,2HCl (170·0) requires C = 28·2; H = 5·3; N = 24·7; Cl = 41·7 per cent.

The solution of the hydrochloride reduces ammoniacal silver nitrate strongly on warming. It gives, with sodium nitroprusside on addition of sodium hydroxide, a brown colour; with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution, a bright yellow colour; on treatment with nitrous acid and addition to sodium-β-naphthoxide, a deep reddish-brown solution; with ferric chloride, no colour; with Fehling's solution, reduction on warming; with potassium permanganate in cold acid solution, instant reduction; with gold chloride, a brown precipitate which dissolves on warming, reduction taking place.

The properties and composition indicate that the substance is correctly formulated as *4-amino-5-methylglyoxaline* (VIII, p. 669).

The *picrate* is sparingly soluble in water, but more readily so in alcohol, from which it separates in old-gold needles, which darken rapidly above 180° and melt at 195° (corr.).

Found: N = 25·3.

$C_4H_7N_3,C_6H_3O_7N_3$ (326·2) requires N = 25·8 per cent.

The *benzylidene* derivative was prepared by treating 0·23 gram of the hydrochloride in 5 c.c. of water with 0·4 gram of sodium acetate and 0·2 c.c. of benzaldehyde. On shaking vigorously, a solid product gradually formed. This was collected and washed with water and ether, in which it is sparingly soluble. It dissolves readily in alcohol, but less so in ethyl acetate, from which it separates in clusters of well-defined needles, which are anhydrous and melt and decompose at 217° (corr.), gradually darkening in colour above 190°.

Found: N = 22·9.

$C_{11}H_{11}N_3$ (185·2) requires N = 22·7 per cent.

The residual liquor from the separation of the 4-amino-5-methylglyoxaline picrate was reconverted into the hydrochloride and evaporated to dryness, when it left about 3 grams of a semi-solid mass, which yielded only ammonium chloride (1·0 gram) on crystallisation from water or alcohol. It was dissolved in water therefore, chlorine determined in an aliquot portion, and the hydrochloric acid in the remainder removed by the addition of the calculated quantity of freshly precipitated silver carbonate. The resulting solution was evaporated to a syrup, mixed with a little alcohol, and kept, when α-alanine gradually separated. This melted, without recrystallisation, at 287° (corr.), a synthetic specimen melting at the same temperature in the same bath, and the mixture of the two showing no depression. The identity was further confirmed by its reactions, analysis, and formation of the

copper salt (Found: C = 40·1; H = 8·1; N = 15·4. $C_3H_7O_2N$ requires C = 40·4; H = 7·9; N = 15·7 per cent.).

Strecker (*Annalen*, 1850, **75**, 36) found that the air-dried copper salt retained one molecule of water of crystallisation. More recently, Zelinsky and Stadnikoff (*Ber.*, 1908, **41**, 2062) failed to confirm this, and described a salt with three molecules of water of crystallisation. Both the acid obtained above and a synthetic specimen of undoubted purity yielded a copper salt with only one molecule of water of crystallisation (Found: Cu = 24·7. $(C_3H_6O_2N)_2Cu,H_2O$ requires Cu = 24·7 per cent.), and the salt did not gain appreciably in weight on keeping for several days in an atmosphere saturated with moisture.

Reduction of 4-p-Bromobenzeneazo-2-methylglyoxaline.

13·2 Grams of bromobenzeneazo-2-methylglyoxaline were triturated with 120 c.c. of cold hydrochloric acid and gradually treated with 72 c.c. of stannous chloride solution, the trituration being continued and the temperature maintained below 10°. The insoluble stannichloride which gradually formed was collected, and the residual liquor freed from tin and evaporated, leaving only 0·3 gram of residue, in which ammonia and *p*-bromoaniline were identified. The insoluble stannichloride was dissolved in water, freed from tin, and the resulting solution evaporated to low bulk, when, on keeping, a quantity of minute needles separated. These dissolved readily in water, but more sparingly in 10 per cent. hydrochloric acid, from which they were obtained in clusters of glistening, elongated, rhombic prisms melting at 273° (corr.).

Found: C = 38·9, 39·6; H = 3·9, 3·9; N = 13·65.

0·2031 gave 0·2178 AgCl + AgBr, 0·2208 being required.

$C_{10}H_{10}ON_3Br,HCl$ (304·55) requires C = 39·4; H = 3·65; N = 13·8 per cent.

The corresponding *base* is precipitated as a mass of minute, colourless needles on treating the concentrated aqueous solution of the hydrochloride with a molecular proportion of sodium hydroxide. It decomposes in warm aqueous solution or on exposure to the air. Dried at 60° in a vacuum, it appears to retain a molecule of water of crystallisation.

Found: C = 42·1, 42·3; H = 4·4, 4·5; N = 14·2; Br = 27·8.

$C_{10}H_{10}ON_3Br,H_2O$ (286·1) requires C = 41·95; H = 4·2; N = 14·7; Br = 27·9 per cent.

The solution of the base gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution. After treatment with nitrous acid in acid solution, a pale yellow colour

develops on addition to sodium-β-naphthoxide. An ammoniacal solution of silver nitrate is reduced in the cold. With Fehling's solution, a bluish-green precipitate is formed, which becomes dark green on warming. With sodium nitroprusside in presence of sodium hydroxide, a reddish-brown colour develops, which changes to green on acidification with acetic acid, and is discharged by excess of the reagent. The aqueous solution reduces cold aqueous acid permanganate. The base reacts with benzaldehyde, with formation of a *benzylidene* derivative, which was not obtained in a crystalline condition. The properties and composition of the base point, therefore, to its being *2-methyl-4-(2′-amino-5′-bromophenyl)-5-glyoxalone* (XII, p. 670).

The *picrate* separates from water in glistening, orange plates which, when dried in the air, melt at 157° (corr.), sintering slightly above 140°. It appears to contain two molecules of water of crystallisation, one of which is lost on drying at 60° in a vacuum.

Found: in air-dried material, N = 15·65; loss at 60° in a vacuum = 3·4. In dried material, N = 16·2.

$C_{10}H_{10}ON_3Br,C_6H_3O_7N_3,2H_2O$ requires N = 15·8. For loss of $1H_2O$, H_2O = 3·4 per cent.

$C_{10}H_{10}ON_3Br,C_6H_3O_7N_3,H_2O$ (515·1) requires N = 16·3 per cent.

After the separation of most of the above hydrochloride, ammonium chloride began to deposit, and a careful fractionation of the mixture revealed that the two products were present in approximately molecular proportions.

Reduction of 4-Benzeneazo-5-methylglyoxaline.

3·7 Grams were triturated with 20 c.c. of hydrochloric acid and treated, as in the previous experiment, with 12 c.c. of stannous chloride solution. The insoluble stannichlorides amounted to 6·8 grams of moist material. Tin was removed, and the resulting solution evaporated under diminished pressure to low bulk, when the hydrochloride of the base, $C_9H_{10}ON_2$ (*loc. cit.*, p. 254), separated, about 1·8 grams being obtained. The mother liquors eventually deposited ammonium chloride, and, on suitable treatment, yielded a small amount of aniline. The more soluble stannichlorides, when treated similarly, yielded a second *hydrochloride*, which separated as a matted mass of minute needles, readily soluble in water but sparingly so in alcohol. After recrystallisation from 10 per cent. hydrochloric acid, it darkened, but did not melt, at 300°. About 1·2 grams were isolated.

Found: C=46·2; H=5·4; N=15·8; Cl=26·6.
$C_{10}H_{11}ON_3,2HCl$ (262·1) requires C=45·8; H=5·0; N=16·0; Cl=27·0 per cent.

The solution of the hydrochloride was strongly acid to litmus. After treatment with nitrous acid, it gave a deep red coloration with sodium-β-naphthoxide. It gave no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution. With sodium nitroprusside in presence of sodium hydroxide, a pale brown colour developed, which changed to green on acidification with acetic acid, and was discharged by excess of the reagent. Potassium permanganate in cold acid solution, and ammoniacal silver nitrate, were both reduced in the cold. The properties and composition of the compound indicate that it is correctly represented as 2-p-*amino-phenyl*-5-*methyl*-4-*glyoxalone* (XVIII, p. 671).

The *benzylidene* derivative was prepared by treating 0·4 gram of the hydrochloride, dissolved in 8 c.c. of water, with 0·45 gram of sodium acetate and 0·4 gram of benzaldehyde. The oily, yellow product, which became crystalline on stirring, was collected and washed with water and with ether, leaving 0·4 gram of material. This decomposed on boiling with water, and dissolved only sparingly in alcohol and ethyl acetate. It was dried at 60° in a vacuum for analysis, and then melted at 156° (corr.), softening above 153°. The figures obtained indicated that it was the *acetate* of the *mono-benzylidene* derivative.

Found: C=68·0; H=5·5; N=12·7.
$C_{17}H_{15}ON_3,C_2H_4O_2$ (337·3) requires C=67·6; H=5·7; N=12·5 per cent.

The mother liquors from the separation of the hydrochloride yielded small quantities of ammonia and aniline on suitable treatment.

Condensation of Acetaldehyde with Phenylcarbamide.

This condensation has been carried out using various conditions. For example, the phenylcarbamide was added slowly, with stirring, to a large excess of freshly distilled aldehyde, or was suspended in alcohol and mixed with aldehyde or acetal in various proportions. In every case the same product was obtained—two molecules of the phenylcarbamide uniting with one of the aldehyde to form *ethylidenebisphenylcarbamide*. This substance is practically insoluble in water, ether, ethyl acetate, or benzene, and very sparingly soluble in alcohol, from which it separates as a felted mass of silky needles melting at 220° (corr.).

Found: C=64·4; H=6·4; N=18·8, 18·9.

$C_{16}H_{18}O_2N_4$ (298·3) requires C=64·4; H=6·2; N=18·8 per cent.

Attempts to obtain partial hydrolysis and subsequent ring closure were unsuccessful.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.1. [*Received, May 5th, 1920.*]

LXXI.—*The Behaviour of Optically Active Esters on Hydrolysis.*

By ALEX. McKENZIE and HENRY WREN.

THE first attempt made by one of us to effect an asymmetric synthesis (T., 1904, **85**, 1249) involved the use of *l*-menthol as the activating agent, and was based on the following lines:

$$C_6H_5{\cdot}CO{\cdot}CO_2H \longrightarrow C_6H_5{\cdot}CO{\cdot}CO_2{\cdot}C_{10}H_{19} \longrightarrow C_6H_5{\cdot}CH(OH){\cdot}CO_2{\cdot}C_{10}H_{19} \longrightarrow C_6H_5{\cdot}CH(OH){\cdot}CO_2H.$$

The failure to realise the synthesis desired was due in this case, as was shown later, to the racemising influence of the alcoholic alkali used in the hydrolysis of the mixture of unequal quantities of the menthyl mandelates.

In the light of recent research (T., 1919, **115**, 602), it was likely that the diastereoisomeric *l*-menthyl mandelates would be catalytically racemised during their hydrolysis, and this point was therefore now examined experimentally. The *l*-menthyl *l*-mandelate used had $[\alpha]_D$ $-137·9°$ in ethyl-alcoholic solution. Of the two active complexes in this ester, the menthyl group undergoes with alkali no optical inversion, whereas inversion does occur with the mandelic group. Accordingly, on hydrolysing the ester with an insufficiency of alcoholic alkali, and then separating the non-hydrolysed ester, the latter was no longer homogeneous, and the value for $[\alpha]_D$ had fallen to $-105°$. A similar examination of the isomeric *l*-menthyl *d*-mandelate gave an interesting result, inasmuch as the catalytic racemisation of this ester led to the production of a solid having a higher activity than that of the original ester; owing to the partial inversion of the *d*-mandelic group, the value for $[\alpha]_D$ in ethyl-alcoholic solution rose from $-9·3°$ in the homogeneous ester to $-51·9°$ in the mixture obtained by the catalytic racemisation. The observation made previously that, when either *l*-menthyl *d*-mandelate or *l*-menthyl *l*-mandelate

is hydrolysed by an excess of alcoholic alkali, the mandelic acid isolated is invariably largely racemised, is now shown to be attended by the catalytic racemisation of the esters during their hydrolysis. The *l*-bornyl mandelates have also been investigated from the same point of view (see experimental part).

The asymmetric synthesis of *l*-atrolactinic acid (T., 1904, **85**, 1249) was successfully accomplished in accordance with the following scheme:

$$C_6H_5\cdot CO\cdot CO_2H \longrightarrow C_6H_5\cdot CO\cdot CO_2\cdot C_{10}H_{19} \longrightarrow$$

$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2\cdot C_{10}H_{19}\end{matrix} \longrightarrow \begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}.$$

From the mixture of unequal quantities of the diastereoisomeric menthyl atrolactinates, a mixture of unequal quantities of the enantiostereoisomeric atrolactinic acids with $[\alpha]_D -9{\cdot}5^\circ$ in ethyl-alcoholic solution was obtained after the complete elimination of the menthol. The *d*-acid was also asymmetrically synthesised (T., 1906, **89**, 365), using pyruvic acid as the starting point:

$$CH_3\cdot CO\cdot CO_2H \longrightarrow CH_3\cdot CO\cdot CO_2\cdot C_{10}H_{19} \longrightarrow$$

$$\begin{matrix}CH_3\\C_6H_5\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2\cdot C_{10}H_{19}\end{matrix} \longrightarrow \begin{matrix}CH_3\\C_6H_5\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix}.$$

Subsequent research has suggested that the success of those syntheses was due to the stability of the atrolactinic complex during the hydrolysis of the menthyl esters, since the labile hydrogen atom in mandelic acid is absent in atrolactinic acid, the stable methyl group being present instead, with the result that desmotropic change does not occur (T., 1915, **107**, 702). The direct proof, however, that this is the correct interpretation was lacking, and it is now submitted in the present paper. *l*-Menthyl *l*-atrolactinate was accordingly prepared, and found to melt at 55·5—56° and to have $[\alpha]_D^{14} -102{\cdot}7^\circ$ in chloroform solution. After hydrolysis by an excess of alcoholic alkali, it gave practically pure *l*-atrolactinic acid. Again, when the ester was hydrolysed with half the quantity of alcoholic alkali requisite for complete hydrolysis, the non-hydrolysed ester gave a value for $[\alpha]_D$ which was not far short of that for the pure ester. Further, the fractional hydrolysis of *l*-menthyl *dl*-atrolactinate was examined in the expectation that the confusing results which have been obtained in other cases with esters containing mobile hydrogen atoms would not be encountered in this case. This expectation was realised. On partial hydrolysis, a lævorotatory acid was obtained from the alkali salts, an indication that *l*-menthyl *l*-atrolactinate is hydrolysed

more quickly than is *l*-menthyl *d*-atrolactinate. The non-hydrolysed ester should, therefore, contain an excess of the *d*-atrolactinate, which, on hydrolysis, should give a dextrorotatory acid, and this was borne out by experiment.

An examination of the hydrolysis of esters of the optically active α-hydroxy-β-phenylpropionic acids was also included in the scope of the present investigation. We had previously shown (T., 1910, **97**, 1355) that those acids can be interconverted, thus:

$$d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \longrightarrow \text{(by } PCl_5\text{)}\ l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H$$

$$\uparrow \text{(by } CaCO_3 \text{ and water)} \qquad\qquad \downarrow \text{(by } CaCO_3 \text{ and water)}$$

$$d\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H\ \text{(by } PCl_5\text{)} \longleftarrow l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

The ease with which the pure hydroxy-acid could be prepared from its enantiostereoisomeride was very striking in this case, and it was apparent that the racemisation phenomena which accompanied on so many occasions the Walden inversions investigated by one of us and his co-workers were much less pronounced than usual. It is, indeed, somewhat remarkable that in the study of the Walden inversion, racemisation occurs so frequently when the displacement is effected with compounds containing a phenyl group in direct attachment to the asymmetric carbon atom. Now, α-hydroxy-β-phenylpropionic acid has the phenyl group separated from the asymmetric atom by a methylene group, and to this circumstance may be ascribed the behaviour of this acid, to which reference has just been made.

The type of racemisation with which one has to deal in connexion with reactions involving displacement of gronps, whether accompanied with configurational change or not, is obviously different from the type when an optically active ester is hydrolysed with an excess of alcoholic alkali. An illustration of this difference is afforded with compounds containing a tertiary asymmetric atom (T., 1910, **97**, 1016). Complete racemisation occurs when the chlorine in *l*-α-chloro-α-phenylpropionic acid is removed by the action of water,

$$l\text{-}\substack{C_6H_5\\CH_3}{>}C{<}\substack{Cl\\CO_2H} \longrightarrow r\text{-}\substack{C_6H_5\\CH_3}{>}C{<}\substack{OH\\CO_2H},$$

whilst a partly racemised atrolactinic acid is formed by the action of water and silver oxide,

$$l\text{-}\substack{C_6H_5\\CH_3}{>}C{<}\substack{Cl\\CO_2H} \longrightarrow r\text{- and } l\text{-}\substack{C_6H_5\\CH_3}{>}C{<}\substack{OH\\CO_2H}.$$

Similarly, by the action of nitrous acid on *l*-α-amino-α-phenylpropionic acid (T., 1912, **101**, 390), the resulting atrolactinic acid is quite inactive,

$$l\text{-}\ {}^{C_6H_5}_{CH_3}{>}C{<}^{NH_2}_{CO_2H} \longrightarrow r\text{-}\ {}^{C_6H_5}_{CH_3}{>}C{<}^{OH}_{CO_2H}.$$

On the one hand, these examples show clearly that the absence of a mobile hydrogen atom in the α-position with respect to the carboxyl group does not prevent racemisation coming into play during the interchange of groups provided that one of the groups attached to the asymmetric atom is the phenyl group. On the other hand, when the behaviour of an ester, such as *l*-menthyl *l*-atrolactinate, towards alcoholic alkali is considered, it is now proved that the active atrolactinic acid can be recovered practically unracemised.

The study of the hydrolysis of esters of optically active α-hydroxy-β-phenylpropionic acid was accordingly made. Ethyl *l*-α-hydroxy-β-phenylpropionate, $C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2Et$, for instance, has a hydrogen atom associated with a hydroxyl group in the α-position relatively to the carbethoxy-group, and in this respect it resembles ethyl *l*-mandelate, the behaviour of which on hydrolysis has been carefully investigated. On the other hand, it differs from ethyl *l*-mandelate in not having its phenyl group attached to the asymmetric atom.

The action of an excess of alkali on *d*-α-hydroxy-β-phenylpropionic acid was accordingly examined, when it was found that the recovered acid was non-racemised (table I), a behaviour different from that of *l*-mandelic acid (T., 1919, **115**, 602). Ethyl *l*-α-hydroxy-β-phenylpropionate was then hydrolysed with an excess of alkali, the results being recorded in table II, from which it will be seen that in each experiment the recovered acid was practically optically pure. Moreover, there was practically no catalytic racemisation on the partial hydrolysis of the same ester with alcoholic alkali, the non-hydrolysed ester having $[\alpha]_D$ −28·0° in carbon disulphide solution, whereas the value for the pure ester is $[\alpha]_D$ −28·8°. *l*-Menthyl *d*-α-hydroxy-β-phenylpropionate was also prepared and examined from the same point of view, in order to contrast it with *l*-menthyl *d*-mandelate.

The difference between the behaviour of the esters of *l*-mandelic acid and *l*-α-hydroxy-β-phenylpropionic acid on hydrolysis is accordingly pronounced. So far as racemisation comes into play in the hydrolysis of an optically active ester by alcoholic alkali, it is now clear that, although compounds of the type $R{\cdot}CH(OH){\cdot}CO_2R'$ present a system prone to racemisation in virtue of the mobile

hydrogen atom being in the α-position, this circumstance is not i itself a factor in promoting racemisation unless R is an aromat residue in direct attachment to the asymmetric atom. In th event of R being an aliphatic group, it may be argued that th system would probably be stable, so far as racemisation by alka is concerned, and there is a certain amount of experimental eviden in favour of this. For example, although it had not been foun possible to effect the asymmetric synthesis of mandelic acid on th lines outlined at the start of this paper, a positive result was reache when the phenyl group was displaced by a methyl one, inasmuc as the asymmetric synthesis of *l*-lactic acid could be accomplishe by the agency of *l*-menthol (T., 1905, **87**, 1373), using pyruvic ac as the starting point,

$$CH_3\cdot CO\cdot CO_2H \longrightarrow CH_3\cdot CO\cdot CO_2\cdot C_{10}H_{19} \longrightarrow$$
$$CH_3\cdot CH(OH)\cdot CO_2\cdot C_{10}H_{19} \longrightarrow CH_3\cdot CH(OH)\cdot CO_2H$$

A similar result was obtained by the use of *l*-borneol (T., 190 **89**, 688), whilst *d*-lactic acid was asymmetrically synthesised b means of *d*-amyl alcohol (T., 1909, **95**, 544). The influence of th phenyl group as compared with the methyl group is thus show clearly, inasmuch as the diastereoisomeric *l*-menthyl lactates a much more stable towards the racemising influence of alcohol alkali than are the diastereoisomeric *l*-menthyl mandelates, sinc from a mixture of *l*-menthyl *d*-lactate and *l*-menthyl *l*-lactate con taining a preponderance of one of them, it was possible to obtai an optically active lactic acid when the ester mixture was com pletely hydrolysed.

β-Hydroxy-β-phenylpropionic acid and tropic acid are isomer with atrolactinic acid and α-hydroxy-β-phenylpropionic acid. Th methyl ester of *d*-β-hydroxy-β-phenylpropionic acid,

$$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H,$$

gives the optically pure *d*-acid on hydrolysis with alcohol potassium hydroxide (T., 1913, **103**, 112), and it will be noted th the hydrogen atom associated with the hydroxy-group is in th case in the β-position, a system which should be stable so far a racemisation of its esters on hydrolysis is concerned, even althoug a phenyl group is attached to the asymmetric atom. On the othe hand, the reverse is the case with tropic acid,

$$C_6H_5\cdot CH(CH_2\cdot OH)\cdot CO_2H,$$

where we have a system which might be expected to behave lik mandelic acid; Gadamer's experiments on the racemisation of eth *d*-tropate on hydrolysis (*J. pr. Chem.*, 1913, [ii], **87**, 312) bear th out.

The behaviour on hydrolysis of the optically active esters of the various isomeric "phenyl-lactic" acids, namely,

$$\begin{matrix}C_6H_5\\CH_3\end{matrix}>C<\begin{matrix}OH\\CO_2H\end{matrix},\quad C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H,$$

$$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H,\quad \begin{matrix}C_6H_5\\OH\cdot CH_2\end{matrix}>C<\begin{matrix}H\\CO_2H\end{matrix},$$

has thus been examined fairly completely.

EXPERIMENTAL.

Catalytic Racemisation of the Diastereoisomeric l-*Menthyl Mandelates.*

The *l*-menthyl *l*-mandelate used had $[\alpha]_D$ $-137 \cdot 9°$ in ethyl-alcoholic solution. Ten c.c. of the solution of sodium in ethyl alcohol employed for its partial hydrolysis required 14·3 c.c. of 0·101*N*-sulphuric acid for neutralisation, and of this solution, 83 c.c. were added to a solution of the ester (7·2 grams) in 100 c.c. of ethyl alcohol. After twenty-two hours at the ordinary temperature, 130 c.c. of ethyl alcohol were removed from the neutral liquid by distillation, and 1·1 grams of sodium salt separated on cooling. The acid obtained from this was a mixture of *r*- and *l*-mandelic acids with $[\alpha]_D$ $-53°$ in ethyl-alcoholic solution, the pure *l*-acid having $[\alpha]_D$ about $-152°$ in the same solvent. After the removal of the sodium salt, the filtrate was evaporated, and the menthol separated from the residue by distillation in a current of steam. The residual solid ester (2·7 grams) gave $[\alpha]_D$ $-105°$ ($c=1 \cdot 6$) in ethyl-alcoholic solution. The solution of sodium salt from which the ester had been separated was then acidified, and the resulting mandelic acid gave $[\alpha]_D$ $-81 \cdot 9°$ in ethyl-alcoholic solution.

An examination of the isomeric *l*-menthyl *d*-mandelate with $[\alpha]_D$ $-9 \cdot 3°$ in ethyl-alcoholic solution was next made. Six grams were dissolved in 96 c.c. of ethyl-alcoholic potassium hydroxide (0·1077*N*), the amount calculated for complete hydrolysis being 192·1 c.c. Thereafter, the liquid was kept for two days at the ordinary temperature, the ethyl alcohol was removed from the neutral solution, and water was then added. The mixture of the non-hydrolysed ester and the menthol was then extracted with ether, whilst the mandelic acid was obtained from the aqueous residue in the customary manner. The fact that the recovered acid had $[\alpha]_D$ $+91 \cdot 2°$ in aqueous solution indicated the presence in it of a considerable quantity of the racemic acid. From the ethereal extract containing the non-hydrolysed ester and menthol, the ether was removed, and the oil distilled in a current of steam

to separate the menthol. The recovered solid ester, which was quite free from uncombined menthol, gave $[\alpha]_D$ $-51{\cdot}9°$ ($c=4{\cdot}171$) in ethyl-alcoholic solution.

Catalytic Racemisation of the Diastereoisomeric l-*Bornyl Mandelates.*

The *l*-bornyl *l*-mandelate used had $[\alpha]_D$ $-86{\cdot}0°$ in ethyl-alcoholic solution (T., 1907, **91**, 789). Nineteen c.c. of an ethyl-alcoholic solution of potassium hydroxide ($0{\cdot}6532N$) were added to a solution of 7·05 grams of the ester in 100 c.c. of ethyl alcohol. The solution was treated as already described for the menthyl *d*-mandelate. The recovered mandelic acid had $[\alpha]_D$ $-106{\cdot}2°$ in aqueous solution, whereas the optically pure acid has a value about 50° higher than this. As was expected, the rotation of the recovered ester was less lævorotatory than that of the homogeneous ester, the value obtained being $[\alpha]_D$ $-58{\cdot}0°$ in ethyl-alcoholic solution.

When a similar experiment was carried out with *l*-bornyl *d*-mandelate, the non-hydrolysed ester had a dextrorotation less than that of the original ester, which had $[\alpha]_D$ $+23{\cdot}0°$ in ethyl-alcoholic solution. The ester (10·3 grams) was dissolved in 146 c.c. of ethyl alcohol, and 28 c.c. of ethyl-alcoholic potassium hydroxide ($0{\cdot}6532N$) were added. The recovered mandelic acid had $[\alpha]_D$ $+105{\cdot}5°$ in aqueous solution, whereas the non-hydrolysed ester had $[\alpha]_D$ $+15{\cdot}3°$ in ethyl-alcoholic solution.

We are indebted to Miss Isobel Agnes Smith for carrying out these experiments with the bornyl mandelates.

Hydrolysis of l-*Menthyl* l-*Atrolactinate.*

l-Atrolactinic acid (T., 1910, **97**, 1016) was esterified by heating on a boiling-water bath for fifteen hours with *l*-menthol and a small quantity of concentrated sulphuric acid. The crude solid ester was finally crystallised from light petroleum at the temperature of a freezing mixture of ice and salt.

l-*Menthyl* l-*atrolactinate*, $\frac{Ph}{Me}{>}C{<}\frac{OH}{CO_2{\cdot}C_{10}H_{19}}$, separates from light petroleum in colourless, silky needles, and melts at 55·5—56°. It is readily soluble in this solvent at the ordinary temperature, and it is also readily soluble in the common organic solvents:

0·1200 gave 0·3300 CO_2 and 0·0997 H_2O. C=75·0; H=9·3.

$C_{19}H_{28}O_3$ requires C=74·9; H=9·3 per cent.

Its specific rotation was determined in the following solvents:

(*a*) Acetone:

$l=2$, $c=1\cdot982$, $\alpha_D^{9\cdot5} - 2\cdot96°$, $[\alpha]_D^{9\cdot5} - 74\cdot7°$.

(*b*) Ethyl alcohol:

$l=2$, $c=1\cdot2741$, $\alpha_D^{10} - 2\cdot30°$, $[\alpha]_D^{10} - 90\cdot3°$.

(*c*) Chloroform:

$l=2$, $c=1\cdot4215$, $\alpha_D^{14} - 2\cdot92°$, $[\alpha]_D^{14} - 102\cdot7°$.

Complete Hydrolysis with Alcoholic Alkali.—The ester (1·6 grams) was dissolved in 40 c.c. of ethyl-alcoholic potassium hydroxide (0·202*N*), the amount calculated for complete hydrolysis being 26 c.c. After four days at the ordinary temperature, the acid was isolated, and its rotation when determined in ethyl-alcoholic solution showed that no racemisation had occurred during the hydrolysis. The value was $[\alpha]_D - 37\cdot2°$ ($c=1\cdot398$). The optically pure acid has $[\alpha]_D - 37\cdot7°$.

Partial Hydrolysis with Alcoholic Alkali.—The ester (1·9 grams) was dissolved in 16 c.c. of ethyl-alcoholic potassium hydroxide (0·193*N*), the quantity calculated for complete hydrolysis being 32·4 c.c. After twenty-four hours at the ordinary temperature, the treatment was similar to that adopted in the experiment with *l*-menthyl *d*-mandelate. The residual ester was not appreciably hydrolysed during the prolonged distillation in a current of steam when the menthol was being removed.

The recovered ester gave $[\alpha]_D - 99\cdot8°$ ($c=1\cdot988$) in chloroform solution.

The recovered acid melted at 114·5—116° (the pure *l*-acid melts at 116—117°); its rotation in ethyl-alcoholic solution gave $[\alpha]_D - 36\cdot1°$ ($c=1\cdot733$).

The optical activity is impaired during the distillation of *l*-menthyl *l*-atrolactinate under diminished pressure. After being distilled twice (b. p. 187·5—188·5°/11 mm.), it readily solidified, and then melted indefinitely at 41—51°, whilst its rotation in chloroform solution gave a low value, namely, $[\alpha]_D - 91\cdot6°$. This product was accordingly hydrolysed with an excess of ethyl-alcoholic potassium hydroxide, and the acid, which was isolated in the usual manner, had $[\alpha]_D - 31\cdot0°$. It appeared probable that the ester had undergone partial racemisation under the influence of heat.

Fractional Hydrolysis of l-*Menthyl* dl-*Atrolactinate.*

l-*Menthyl* dl-*atrolactinate*, prepared by the esterification of anhydrous *r*-atrolactinic acid by heating with menthol and a small

quantity of concentrated sulphuric acid on a boiling-water bath for twenty-five hours, is a colourless oil which boils at 194—194·5°/ 11 mm.:

0·1329 gave 0·3663 CO_2 and 0·1119 H_2O. C=75·2; H=9·4.

$C_{19}H_{28}O_3$ requires C=74·9; H=9·3 per cent.

The following determinations of its specific rotation were made:

(*a*) Carbon disulphide:

$l=2,\ c=2·408,\ \alpha_D^{9} -2·69°,\ [\alpha]_D^{9} -55·9°.$

(*b*) Benzene:

$l=2,\ c=2·1225,\ \alpha_D^{15} -2·71°,\ [\alpha]_D^{15} -63·8°.$

(*c*) Acetone:

$l=2,\ c=2·039,\ \alpha_D^{14} -2·70°,\ [\alpha]_D^{14} -66·2°.$

(*d*) Chloroform:

$l=2,\ c=2·014,\ \alpha_D^{11} -2·80°,\ [\alpha]_D^{11} -69·5°.$

(*e*) Ethyl alcohol:

$l=2,\ c=2·3955,\ \alpha_D^{15} -3·45°,\ [\alpha]_D^{15} -72·0°.$

A solution of the ester (2 grams) in 20 c.c. of ethyl-alcoholic potassium hydroxide (0·93*N*) was boiled for one hour, the amount of alkali requisite for the complete hydrolysis being 7·1 c.c. The acid isolated was optically inactive.

The fractional hydrolysis was conducted with 4 grams of the ester to which 7·1 c.c. of ethyl-alcoholic potassium hydroxide (0·93*N*) were added, this being half of the amount necessary for complete hydrolysis. Boiling of the solution was maintained for two hours. The acid obtained from the potassium salt after separation from menthol and menthyl esters amounted to 0·8759 gram, and it had $[\alpha]_D$ −1·7° in ethyl-alcoholic solution. The hydrolysis of the residual menthyl esters was then completed with 15 c.c. of ethyl-alcoholic alkali (0·93*N*). The resulting acid (0·8394 gram) was dextrorotatory, having $[\alpha]_D$ +2·3° in ethyl-alcoholic solution.

Action of Potassium Hydroxide on d-*α-Hydroxy-β-phenylpropionic Acid.*

d-α-Hydroxy-β-phenylpropionic acid (T., 1910, **97**, 1355) was treated under various conditions with an excess of potassium hydroxide dissolved in water or in ethyl alcohol. The solution was then neutralised, water added, and the ethyl alcohol expelled. The recovered acid was examined polarimetrically in ethyl-alcoholic solution. The pure *d*-acid has $[\alpha]_D$ +18·5° (*loc. cit.*).

TABLE I.

0·83 Gram of acid was taken in each experiment. In order to neutralise this, 5·4 c.c. of alkali (0·93*N*) are required.

Alkali (0·93*N*).	Conditions.	$[\alpha]_D$ of recovered acid.
60 c.c. aqueous.	15 days at ord. temp.	+18·3° (*c* = 3·24)
,,	20 hours at 70°.	18·3° (*c* = 3·44)
60 c.c. alcoholic.	15 days at ord. temp.	18·0° (*c* = 3·14)
,,	20 hours at 70°.	18·2° (*c* = 3·49)

Hydrolysis of Ethyl l-*α-Hydroxy-β-phenylpropionate.*

The *l*-acid was converted into its ethyl ester, which, after crystallisation from light petroleum (b. p. 60—80°), gave the value $[\alpha]_D^{18·5}$ −23·1° in benzene solution, whereas the value previously quoted is $[\alpha]_D$ −22·6° (T., 1911, **99**, 1922). A somewhat higher value is obtained when carbon disulphide is used as the solvent:

$$l=2,\ c=2·306,\ \alpha_D^{18}\ -1·33°,\ [\alpha]_D^{18}-28·8°.$$

Complete Hydrolysis.—The results obtained by hydrolysing the ester with a slight excess of aqueous or alcoholic alkali are expressed in the following table.

TABLE II.

Ester. Grams.	Alkali.	Alkali required. c.c.	Conditions.	$[\alpha]_D$ of recovered acid.
1·0247	6·2 c.c. aqueous (0·93*N*).	5·7	3 hours at 70°.	−17·9° (*c* = 4·04)
0·8696	10 c.c. alcoholic (0·93*N*).	4·8	1 day at ord. temp.	18·0° (*c* = 2·67)
0·8696	10 c.c. alcoholic (0·93*N*).	4·8	2½ hours at 70°.	17·9° (*c* = 2·28)
0·9957	47 c.c. alcoholic (0·1105*N*).	46·4	3 hours at 70°	17·9° (*c* = 3·85)

Partial Hydrolysis with Alcoholic Alkali.—The ester (4 grams) was dissolved in 94 c.c. of ethyl-alcoholic potassium hydroxide (0·1105*N*), the quantity required for complete hydrolysis being 187 c.c.

The solution was divided into two equal parts: (*a*) Kept at the ordinary temperature for twenty-four hours, at the end of which time the solution was neutral. The alcohol was removed by evaporation, water added, and the non-hydrolysed ester extracted with ether. The aqueous solution was then acidified, and the hydroxy-acid extracted with ether. The recovered ester gave the value $[\alpha]_D$ −28·0° for *c*=3·889 in carbon disulphide solution, whilst

the recovered acid gave $[\alpha]_D$ $-17{\cdot}8°$ for $c=3{\cdot}262$ in ethyl-alcoholic solution.

(*b*) Heated at 70° for five hours. The recovered ester had $[\alpha]_D$ $-28{\cdot}3°$ for $c=2{\cdot}226$ in carbon disulphide solution, whilst the recovered acid had $[\alpha]_D$ $-18{\cdot}2°$ for $c=3{\cdot}777$ in ethyl-alcoholic solution.

Hydrolysis of l-*Menthyl* d-*α-Hydroxy-β-phenylpropionate.*

d-α-Hydroxy-β-phenylpropionic acid was esterified by heating with *l*-menthol for seven hours at 120—130° in an intermittent current of hydrogen chloride. The resulting ester was separated from acid and menthol, and purified by crystallisation from light petroleum (b. p. 40—60°).

l-*Menthyl* d-*α-hydroxy-β-phenylpropionate*,

$$C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2{\cdot}C_{10}H_{19},$$

separates from light petroleum (with which it readily forms supersaturated solutions) in matted aggregates of silky needles; it is readily soluble in the hot and sparingly so in the cold solvent. It is also readily soluble in the common organic solvents. It melts at 63—63·5°:

0·1114 gave 0·3070 CO_2 and 0·0923 H_2O. C=75·2; H=9·3.

$C_{19}H_{28}O_3$ requires C=74·9; H=9·3 per cent.

The specific rotation was determined in various solvents:

(*a*) Benzene:

$$l=2,\ c=1{\cdot}4005,\ \alpha_D^{17}\ -0{\cdot}76°,\ [\alpha]_D^{17}\ -27{\cdot}1°.$$

(*b*) Chloroform:

$$l=2,\ c=2{\cdot}697,\ \alpha_D^{15\cdot5}\ -1{\cdot}99°,\ [\alpha]_D^{15\cdot5}\ -36{\cdot}9°.$$

(*c*) Acetone:

$$l=2,\ c=0{\cdot}871,\ \alpha_D\ -0{\cdot}86°,\ [\alpha]_D\ -49{\cdot}4°.$$

The ester (1·1 grams) was dissolved in 40 c.c. of ethyl-alcoholic potassium hydroxide (0·1105*N*), the amount calculated for complete hydrolysis being 33 c.c. After eight hours at 70°, the acid was isolated. It melted at 121—123·5°, whereas the pure *d*-acid melts at 124—125°. That very slight racemisation had occurred during the hydrolysis is indicated by the somewhat low value for the specific rotation in ethyl-alcoholic solution, namely, $[\alpha]_D$ $+17{\cdot}0°$ ($c=2{\cdot}586$).

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LXXII.—*The Use of αβ-Dichlorovinyl Ethyl Ether for the Production of Chloroacetates and Acid Chlorides.*

By HOLLAND CROMPTON and PAULE LAURE VANDERSTICHELE.

THE production of ethyl chloroacetate, and eventually of chloroacetic acid, by the action of water on $\alpha\beta$-dichlorovinyl ethyl ether ıas been the subject of a large number of patents. By using dry ıydrogen chloride in place of water, chloroacetyl chloride is obtained (D.R.-P. 222194), and Imbert found (D.R.-P. 212592) hat dichlorovinyl ethyl ether and ethyl alcohol react, with the production of ethyl chloroacetate and ethyl chloride:

$$\mathrm{CHCl{:}CCl{\cdot}OEt + EtOH = CH_2Cl{\cdot}CO_2Et + EtCl.}$$

He also states that methyl chloroacetate is formed if methyl ılcohol is used in place of ethyl alcohol.

We find that $\alpha\beta$-dichlorovinyl ethyl ether enters into a large ıumber of reactions of the above type. It is attacked, and usually vith great readiness, when heated with alcohols, phenols, or acids. Action is of two kinds:

$$\mathrm{CHCl{:}CCl{\cdot}OEt + ROH} \begin{cases} \nearrow \mathrm{CH_2Cl{\cdot}CO_2R + EtCl} \quad (1) \\ \searrow \mathrm{CH_2Cl{\cdot}CO_2Et + RCl} \quad (2) \end{cases}$$

nd it seems likely that an additive compound,

$$\mathrm{CH_2Cl{\cdot}CCl(OEt){\cdot}OR,}$$

s first formed, which decomposes into the products (1) and (2). Our experience is that alcohols give the products of both reactions, ut that (1) predominates, except in the case of methyl alcohol. Phenols give the products of (1) only, and usually in excellent ield. Acids react mainly in accordance with (2), the products eing ethyl chloroacetate and an acid chloride. The yields are ariable, but it would appear that reactions of the above type ould be used in certain cases for the production of chloroacetates r acid chlorides.

To prepare $\alpha\beta$-dichlorovinyl ethyl ether, sodium is dissolved in ry alcohol in sufficient quantity to form a saturated solution of odium ethoxide. Trichloroethylene is then added in the proportion of one molecule of trichloroethylene to one and a-half atoms f sodium. Heat is applied until action commences, when further eating is unnecessary. The product, when cold, is mixed with large volume of distilled water, and the oil which separates is ashed, dried with calcium chloride, and rectified. The main

portion distils at 122—126°, and this is nearly pure dichlorovinyl ethyl ether. The yield is about 70 per cent. of the theoretical.

For the action on alcohols or phenols, the substance was employed in as dry a state as possible and mixed with the ether in equivalent quantity. Heat was applied to start the reaction, but further heating was often unnecessary, except towards the end of the process. In other cases, however, heat had to be applied throughout to maintain the reaction. The products were separated by fractional distillation, or, where possible, by crystallisation. The chloroacetate of the alcohol or phenol radicle was finally identified by analysis. Ethyl chloroacetate was recognised by heating the appropriate fraction with aniline, thus forming the characteristic ester of phenylglycine.

The results with methyl alcohol were not in accordance with Imbert's statement. Ethyl chloroacetate was the main product and methyl chloroacetate was only produced in relatively small quantity. Ethyl alcohol gave the expected excellent yield of ethyl chloroacetate. *iso*Amyl, heptyl, allyl, and menthyl alcohols were each found to yield the chloroacetate of the alcohol radicle, but ethyl chloroacetate was also formed in these cases. With glycerol and mannitol, no uniform product could be obtained.

All the phenols examined gave good yields of the aryl chloroacetate, but in no case was ethyl chloroacetate detected. The compounds dealt with were phenol, *o*-cresol, guaiacol, α- and β-naphthol, resorcinol, and quinol. The two latter compounds gave the bischloroacetates. *β-Naphthyl chloroacetate*, $C_{12}H_9O_2Cl$, which has not been previously described, crystallises in small, colourless leaflets melting at 95°. It dissolves readily in hot alcohol, and is much less soluble in the cold.

The monobasic acids, the behaviour of which with dichlorovinyl ethyl ether was examined, were acetic, chloroacetic, phenylacetic, benzoic, anisic, and α-naphthoic. In most cases action occurred readily on heating, but it was necessary to apply heat continuously throughout the process. Some hydrogen chloride was evolved in each case, but ethyl chloride was only observed in the case of anisic acid and of naphthoic acid. Ethyl chloroacetate was always present as the chief product of the reaction. The acid chloride formed at the same time was isolated in a pure state in the reactions with acetic, chloroacetic, and benzoic acids. In the other cases, the acid chloride was not obtained pure, but its presence was indicated by the immediate production of the corresponding amide on treating the appropriate fraction with ammonia.

Two dicarboxylic acids, oxalic and succinic, were also dealt with. Ethyl chloroacetate was formed in quantity in each case, but the

acid chloride was not obtained, succinic acid being almost entirely converted into succinic anhydride. This may be explained by the reaction taking place in stages, the monochloride of the acid being first formed. The monochloride of oxalic acid, as Staudinger has pointed out (*Ber.*, 1908, **41**, 3558), is extraordinarily unstable and decomposes at once into hydrogen chloride, carbon monoxide, and carbon dioxide. The monochloride of succinic acid would naturally pass into succinic anhydride.

BEDFORD COLLEGE,
REGENT'S PARK, N.W. 1. [*Received, March 9th*, 1920.]

LXXIII.—*Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide.*

By LANCELOT SALISBURY BAGSTER and GEORGE COOLING.

THE work to be described in this paper was suggested by some results previously published by Bagster and Steele (*Trans. Faraday Soc.*, 1912, **8**, 51), who found that, although dry solutions of hydrogen bromide in liquid sulphur dioxide were practically non-conducting, the addition of water, which itself in solution is also non-conducting, allowed current to flow freely, hydrogen being discharged at the cathode and bromine at the anode, whilst water was carried from anode to cathode and deposited there. The conclusion drawn was that combination between the two solutes preceded conduction, and comparison with the similar behaviour of organic compounds led to the suggestion that the water and hydrogen bromide united to form an oxonium compound which was electrolytic in character.

The present work was undertaken in order to examine the nature of this phenomenon carefully, and in particular to obtain quantitative information regarding the products formed during electrolysis and regarding the compound from which the products are derived. As an alternative explanation to that already offered, it may be suggested that a simple hydrate type of compound is formed analogous to $CuSO_4,5H_2O$, and that the deposition of water at the cathode is brought about during electrolysis by the loss of the hydrogen bromide holding it in solution. The experimental evidence, however, renders this suggestion untenable.

The experiments to be described were carried out at the temperature of boiling liquid ammonia, which was used as

refrigerant. The solutions were prepared and the experiments carried out in large test-tubes immersed in the ammonia contained in Dewar flasks. The tubes were closed by rubber stoppers carrying the electrodes and tubes for introducing the gaseous sulphur dioxide, which condensed to liquid at the temperature of the ammonia. Water was placed in the tube before placing the latter in the ammonia. The water remained as a solid at the bottom of the test-tube after the introduction of the sulphur dioxide, but on passing gaseous hydrogen bromide into the liquid, two layers were formed, the lower one consisting of a solution of sulphur dioxide and hydrogen bromide in water, and the upper one of a solution of water and hydrogen bromide in sulphur dioxide.

In the course of preliminary experiments, it was found that if the upper layer were syphoned off and used for the electrolysis, the current soon fell in value, whilst no water was deposited at the cathode, sulphur being liberated there in quantity. When the lower layer was allowed to remain in the vessel during the electrolysis, the current maintained its initial value, whilst water appeared at the cathode, very little sulphur being deposited. The water deposited at the cathode collected as small drops, which fell to the bottom of the apparatus.

The probable explanation of the need for the presence of the second layer is that it serves to maintain a saturated solution, and that otherwise the solution near the electrodes becomes depleted of water and hydrogen bromide, a different type of reaction then setting in. In the electrolysis experiments to be described, the second layer was present, but the electrodes were so arranged that conduction and electrolysis took place in the upper solution with the sulphur dioxide as solvent.

Two series of quantitative investigations were carried out, namely, (1) solubility determinations, and (2) determination of the quantity of water deposited at the cathode. In both cases the following method of analysis was adopted for the mixtures and solutions obtained, which contained water, sulphur dioxide, and hydrogen bromide. The sample was introduced into a weighed vessel, and most of the sulphur dioxide and some of the hydrogen bromide boiled off at a temperature below 0°, the gases being absorbed in sodium hydroxide solution. The bromide and sulphite in the hydroxide solution were determined by standard methods. Trial showed that the water was not appreciably distilled and could be estimated in the residue. For this purpose, a weighed quantity of concentrated sodium hydroxide solution was added to the already weighed vessel containing the water and residual sulphur dioxide and hydrogen bromide, the vessel then being re-

weighed. A determination of the bromide and sulphite in the solution enabled the water to be calculated by difference. Tests with known quantities of the constituents showed that the method was accurate to about 1 per cent.

For the *solubility determinations*, the solutions were prepared by adding excess of water to the sulphur dioxide and passing into the liquid varying amounts of hydrogen bromide. The solutions were well shaken and allowed to settle, the clear, upper layer being syphoned off for analysis. The results of the analyses are given in the following table:

Hydrogen bromide. Gram.	Water. Gram.	Gram-mol. of hydrogen bromide.	Gram-mol. of water.	Dissolved in *x* grams of sulphur dioxide.
0·568	0·126	0·0070	0·0070	10·2
0·970	0·214	0·0120	0·0119	15·6
0·435	0·096	0·0054	0·0053	11·0
0·650	0·145	0·0080	0·0080	9·7

It will be seen that the water and hydrogen bromide are found in the solutions in equimolecular proportion, and as water itself is but sparingly soluble in sulphur dioxide, it may be concluded that a compound, H_2O,HBr, is formed. Whether this compound is an oxonium derivative or a simple hydrate can be decided from observation during electrolysis. If the deposit of water at the cathode were formed by precipitation of dissolved water as the hydrogen bromide holding it in solution was destroyed by electrolysis, a similar deposit should appear at the anode. In no case was the slightest indication of such deposit observed, and it may be concluded that a true oxonium compound is formed:

$$H_2O + HBr \rightleftharpoons {}^{H}_{H}{>}O{<}^{H}_{Br},$$

and as the hydrogen and water liberated during electrolysis both appear at the cathode, this compound must ionise as follows:

$${}^{H}_{H}{>}O{<}^{H}_{Br} \rightleftharpoons \left({}^{H}_{H}{>}O{<}^{H}\right)^{\cdot} + \overset{-}{Br}$$

the H_3O' ion losing its charge at the electrode during electrolysis and forming hydrogen and water.

This formula and mechanism of reaction have been previously suggested by Bagster and Steele, but no quantitative evidence was available, and the formula adopted was based on speculation. It was also shown in the paper referred to that Faraday's law holds for solutions in sulphur dioxide, and it is to be expected that the water and hydrogen liberated will correspond with the quantity of silver deposited in a silver voltameter. It was shown, however,

that in the case of the hydrogen this expectation was not realised, and further careful experiments lately carried out gave no better result. As the solutions were always coloured yellow, probably by traces of bromine, it is probable that the hydrogen was destroyed by reaction at the electrode. The water deposited, however, has been estimated, and found to correspond closely with the quantity predicted by the theory put forward. For this determination, the cathode consisted of a platinum wire sealed through the bottom of a glass tube, the deposited water being collected in a small glass cup suspended underneath. At the end of the experiment, the cup was transferred to the weighed vessel and its contents analysed, as already described.

Two experiments were carried out, with the following results:

Silver in voltameter. Gram.	Water deposited. Gram.	Milligram equivalent of silver.	Milligram equivalent of water.
0·120	0·022	1·11	1·22
0·224	0·037	2·08	2·06

It will be seen from the results that one equivalent of water is liberated at the cathode in the sulphur dioxide solution for every equivalent of silver deposited in the voltameter. This is the result to be expected if the explanation offered as to the mechanism of reaction is correct.

This work has seemed of sufficient importance to publish, as it is probable that similar compounds exist in aqueous solutions of halogen hydrides, quite apart from hydrates of the ordinary type, and that they may take part in the electrolysis and reactions of such solutions.

THE UNIVERSITY OF QUEENSLAND,
BRISBANE. [*Received, May 1st*, 1920.]

LXXIV.—*Some Properties of Benzanthrone.*

By ARTHUR GEORGE PERKIN.

DURING some experiments with benzanthrone, attention was arrested by the deep blood-red coloration which it yields when dissolved in concentrated sulphuric acid. As the addition of water to this solution reprecipitates quantitatively unchanged benzanthrone, there thus seemed evidence of the formation of an oxonium salt. On diluting the acid solution with acetic acid, or by adding sulphuric acid to benzanthrone dissolved in acetic acid,

however, no insoluble compound of this nature could be isolated. In attempting again to prepare a ferrichloride by the addition of anhydrous ferric chloride to an acetic acid solution of benzanthrone, diluted with a few drops of hydrochloric acid, only the unchanged substance separated on cooling, but on reducing the amount of hydrochloric acid to a minute proportion, red needles were at first deposited, although these gradually became yellow owing to re-conversion into benzanthrone. Ultimately, it was ascertained that, by avoiding the addition of hydrochloric acid, the desired compound could be readily prepared. To a solution of 0·5 gram of benzanthrone in 20 c.c. of glacial acetic acid, 0·5 gram of anhydrous ferric chloride in the minimum of boiling acetic acid was added. The deep brown liquid, on partial cooling, became semi-solid, owing to the separation of red needles of the *ferrichloride*, and these were collected, washed with acetic acid, and dried at 100°. As the product on treatment with water was readily converted into benzanthrone, this reaction was employed for analytical purposes.

Found: $C_{17}H_{10}O=69·5$, $69·8$; $Fe=8·80$; $Cl=21·7$.

$(C_{17}H_{10}O)_2HFeCl_4$ requires $C_{17}H_{10}O=69·8$; $Fe=8·49$; $Cl=21·54$ per cent.

The *stannichloride*, prepared from benzanthrone (1 gram), acetic acid (15 c.c.), and fuming stannic chloride (1 gram), gave in a similar way a deposit of bright red needles, which when dry had a scarlet appearance. As the substance is apt to darken and become viscid when dried at 100° while moist with acetic acid, it was preferably submitted to a preliminary treatment in a vacuum.

Found: $C_{17}H_{10}O=64·23$, $64·24$.

$(C_{17}H_{10}O)_2SnCl_4$ requires $C_{17}H_{10}O=63·8$ per cent.

The *platinichloride* separates at once as a brick-red, semicrystalline deposit, and this is also readily dissociated by water.

Found: $C_{17}H_{10}O=53·4$; $Pt=22·85$.

$(C_{17}H_{10}O)_2H_2PtCl_6$ requires $C_{17}H_{10}O=52·88$; $Pt=22·42$ per cent.

Having thus ascertained that benzanthrone readily yields salts of this character, it appeared interesting to study the behaviour of one or other of its hydroxy-derivatives in this respect, and certain of these are briefly described in the patent literature (Badische Anilin- & Soda-Fabrik, D.R.-P. 187495). Whereas benzanthrone is prepared by the action of glycerol and sulphuric acid on anthranol, the hydroxybenzanthrones are obtained in a similar way from the hydroxyanthranols, and that which is described as being produced from the 2-hydroxy-compound was selected at first for experiment. Following the directions given

for the preparation of this compound, the product consisted of a greenish-black powder, and could not, apparently, be crystallised. It was ascertained, however, that if a concentrated alcoholic extract of the material is poured into much ether, the main impurity separates as a dark-coloured, viscid mass, and that when the clear liquid, well washed with water, was evaporated, the hydroxy compound remains as nodules in a comparatively pure form. For complete purification it was acetylated, and the crystals obtained by diluting the acetic anhydride solution with alcohol were recrystallised from a mixture of alcohol and acetic acid until they possessed the correct melting point of 200—201°.

When, for the purpose of hydrolysis, the acetyl compound, dissolved in boiling acetic acid, was treated with a few drops of sulphuric acid, scarlet needles, evidently the *sulphate* of the hydroxybenzanthrone, soon separated. These were collected, washed with acetic acid, and dried at 100°.

Found: C=59·04; H=3·37.

$C_{17}H_{10}O_2,H_2SO_4$ requires C=59·30; H=3·48 per cent.

On treatment with water, the sulphate is at once converted into the free hydroxybenzanthrone, a substance which is not readily crystallised, although from nitrobenzene it could be obtained as minute, microscopic needles.

Employing the haloid acids for the hydrolysis of the acetyl compound, oxonium salts could not be isolated.

Methoxybenzanthrone was readily obtained by suspending the hydroxybenzanthrone in methyl alcohol and adding methyl sulphate and methyl-alcoholic potassium hydroxide until no colour change was produced by the latter. It was isolated from the solution by means of water, washed with dilute alkali, and purified by crystallisation, first from alcohol and subsequently from benzene. The fine, yellow needles obtained in this way melted at 198—199° and dissolved in both nitric and sulphuric acids, with the formation of green, fluorescent liquids.

Found: C=83·27; H=4·6.

$C_{18}H_{12}O_2$ requires C=83·07; H=4·6 per cent.

When a boiling acetic acid solution of methoxybenzanthrone is treated with a little sulphuric acid, fine, scarlet needles of the *sulphate* separated, and these were collected and washed with acetic acid.

Found: $C_{18}H_{12}O_2$=72·02; S=8·79.

$C_{18}H_{12}O_2,H_2SO_4$ requires $C_{18}H_{12}O_2$=72·62; S=8·93 per cent.

The *hydrobromide* and *hydrochloride* were obtained in a similar

manner as red needles, but, being unstable at 100°, were not submitted to analysis.

The *ferrichloride*, prepared by means of anhydrous ferric chloride and acetic acid without using hydrochloric acid,* separated immediately in fine, red needles. These, after being collected while hot and washed with acetic acid, formed a maroon-coloured

* The formation of the metallic oxonium salts here described is interesting as addition of hydrochloric acid in these cases is unnecessary and indeed objectionable, at least in the case of its aqueous solution. That required for reaction evidently originates from the conversion in part of the metallic chlorids by means of the acetic acid either into acetate or chloride-acetate. That such a method of procedure is generally adaptable for this purpose appeared likely and experiment has shown that it can be successfully employed for the preparation of oxonium salts of this character from certain xanthone and flavone derivatives. Thus euxanthone diethyl ether in boiling acetic acid solution gives a *platinichloride*, as an orange-coloured, glistening mass of flat needles or leaflets readily dissociated in contact with warm water.

Found: Pt = 19·92.

$(C_{17}H_{16}O_4)_2H_2PtCl_6$ requires Pt = 19·93 per cent.

The *ferrichloride* consists of long, orange-yellow needles.

Found: $C_{17}H_{14}O_4$ = 58·7; Cl = 29·39.

$C_{17}H_{16}O_4,HFeCl_4$ requires $C_{17}H_{16}O_4$ = 58·79; Cl = 29·39 per cent.

Apigenin triethyl ether ferrichloride forms orange-yellow needles, somewhat soluble in hot acetic acid.

Found: $C_{21}H_{22}O_5$ = 78·02.

$(C_{21}H_{22}O_5)_2HFeCl_4$ requires $C_{21}H_{22}O_5$ = 78·05 per cent.,

and the *platinichloride* separates in minute needles of a similar colour.

Found: Pt = 17·33.

$(C_{21}H_{22}O_5)_2H_2PtCl_6$ requires Pt = 17·44 per cent.

Luteolin tetraethyl ether platinichloride is first deposited in the amorphous condition, but this gradually becomes crystalline when the boiling is continued for a short period.

Found: Pt = 16·5.

$(C_{23}H_{26}O_6)_2H_2PtCl_6$ requires Pt = 16·18 per cent.

Myricetin hexaethyl ether platinichloride separates in glistening, orange-coloured, rectangular plates.

Found: Pt = 14·15.

$(C_{27}H_{34}O_8)_2H_2PtCl_6$ requires Pt = 14·11 per cent.

Luteolin tetraethyl ether ferrichloride, (*a*) evidently $(C_{23}H_{26}O_6)_2HFeCl_4$, and the corresponding *myricetin* salt, (*b*) $(C_{27}H_{34}O_8)_2HFeCl_4$, both crystallise in orange-coloured needles, but, being somewhat soluble in acetic acid, hardly separate until the solution is cold. On this account these and other readily soluble compounds of the same character could not be isolated in a completely pure condition owing to the simultaneous deposition at this temperature of a trace of uncombined ferric salt. The yields of the regenerated ethyl ether, obtained by means of water were thus too low.

Found: (*a*) $C_{23}H_{26}O_6$ = 76·8. Calc. 80·0 per cent.

(*b*) $C_{27}H_{34}O_8$ = 67·5. Calc. 83·0 per cent.

glistening mass, and were readily decomposed in contact with water.

Found: $C_{18}H_{12}O_2 = 72{\cdot}40$.

$(C_{18}H_{12}O_2)_2HFeCl_4$ requires $C_{18}H_{12}O_2 = 72{\cdot}32$ per cent.

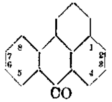
The *platinichloride*, similarly obtained, was scarlet.

Found: $Pt = 21{\cdot}26$.

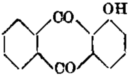
$(C_{18}H_{12}O_2)_2H_2PtCl_6$ requires $Pt = 20{\cdot}97$ per cent.

When methoxybenzanthrone dissolved in acetic acid was treated with chromic acid, an energetic reaction occurred, and by adding water to the solution, a small amount of a crystalline precipitate separated. This was collected, digested with hot dilute ammonia, and the extract neutralised with acid. On keeping, colourless, hair-like needles were deposited, and these, on heating, sintered at 265° and melted at 274—275° with evolution of gas. It at first suggested itself that this compound, which is evidently a *m*-methoxyanthraquinone-*o*-carboxylic acid, would be of service for ascertaining the position, apparently unknown, of the hydroxyl group in this and other hydroxybenzanthrones. Such an idea was, however, abandoned, as no account could be found in the literature of *m*-hydroxyanthraquinone-*o*-carboxylic acids, prepared by other methods, which might be identical or otherwise with the acid in question. Again, the yield of the latter was far from satisfactory.

In considering the constitution of this hydroxybenzanthrone derived from 2-hydroxyanthranol, four distinct positions, namely, 2, 3, 6, 7 (I), for the hydroxyl group at first appear applicable.

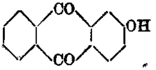


(I.)

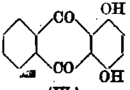


(II.)

On the other hand, as it seems certain that the benzanthrone condensation proceeds similarly in the case of other hydroxyanthranols, the matter is in reality less complex. Thus the fact that 1-hydroxyanthraquinone (II) or the corresponding anthranol yields, according to the literature (*loc. cit.*), an hydroxybenzanthrone of



(III.)



(IV.)

very similar properties to that derived from 2-hydroxyanthraquinone (III), renders the position 2 impracticable for the hydroxyl group present in the latter. Again, by a similar reasoning, the position 3 is not applicable, in that a dihydroxybenzanthrone can be prepared also from quinizarin (IV) or its leuco-compound (*loc. cit.*). Such being the case, the hydroxybenzanthrone under discussion, originating from 2-hydroxyanthranol, must contain the hydroxyl group in the position 6 or 7.

It appeared possible that a solution of this question might be arrived at from a study of the *o*-dihydroxybenzanthrone which has been obtained by the action of glycerol and sulphuric acid on deoxyalizarin (the anthranol corresponding with alizarin), and the examination of this compound was also of interest in that only a meagre account of its properties is to be found in the patent literature (*loc. cit.*).

The product, obtained in the usual manner by the interaction of deoxyalizarin, glycerol, and sulphuric acid, which consisted of a black, resinous powder, was extracted with alcohol, the extract evaporated to a small bulk, and poured into much ether. The clear liquid, decanted from a deposit of tarry impurity, was repeatedly washed with water and evaporated to dryness. The residue, which consisted of crystalline specks admixed with resinous matter, was triturated two or three times with a little ether, collected, and washed with the same solvent. The dull reddish-orange product was now digested with boiling acetic anhydride, the solution diluted with alcohol, and, after keeping overnight, the crystals which had then separated were collected and recrystallised from acetone.

Found: C=73·08; H=4·27.

$C_{21}H_{14}O_5$ requires C=72·83; H=4·05 per cent.

This *diacetoxybenzanthrone*, which has not been previously described, consists of pale yellow needles melting at 199—201°.

When a boiling solution of this compound in acetic acid is treated with sulphuric acid, the liquid becomes blood-red, and dark maroon needles of the *sulphate* of dihydroxybenzanthrone soon separate. These, when dry, appear almost black and closely resemble naphthazarin in appearance. In contact with water, they are slowly decomposed, being converted into minute, orange-red needles of the dihydroxy-compound.

Found: $C_{17}H_{10}O_3$=72·02; S=8·79.

$C_{17}H_{10}O_3,H_2SO_4$ requires $C_{17}H_{10}O_3$=72·77; S=8·88 per cent.

The *hydrobromide*, which is obtained in a similar way from the acetyl compound, separates in glistening, hair-like needles of a

deep maroon colour. On heating at 100°, it is slowly decomposed, and was therefore analysed indirectly by decomposing the product still moist with acetic acid by means of water, and estimating the regenerated dihydroxy-compound and the hydrobromic acid thus produced.

Found: 0·6495 gram of $C_{17}H_{10}O_3$, which corresponds with 0·8503 gram of $C_{17}H_{10}O_3$,HBr, and bromine equivalent to 23·28 per cent. of the latter. Theory requires Br = 23·32 per cent.

The *hydrochloride* and *hydriodide* were also prepared. These closely resembled the hydrobromide, but were not analysed.

The dihydroxybenzanthrone obtained by the hydrolysis of the acetyl derivative crystallised from alcohol, in which it is sparingly soluble, in minute, orange-red plates or leaflets, melting and decomposing at about 309—310°.

Found: C = 78·1; H = 4·07.

$C_{17}H_{10}O_3$ requires C = 77·86; H = 3·81 per cent.

This compound, for which the name *benzalizarin* is suggested, and is here referred to as such, resembles alizarin itself in many of its properties. It is soluble in concentrated sodium hydroxide solution with a pure blue colour, and this, on dilution with much water, gradually becomes dull violet, and finally brown, owing to oxidation. Addition of barium chloride to the blue alkaline solution causes the precipitation of the barium compound as a violet powder. Sulphuric acid dissolves it with a crimson, nitric acid with a bluish-violet, and alcoholic ferric chloride with a yellowish-brown, tint. Dyeing experiments, employing mordanted woollen cloth, indicated that benzalizarin dyes with this material shades which, with the exception of that given by the iron mordant, are identical in character with those given by alizarin itself, although they possess a slightly more orange tint.

	Cr.	Al.	Sn.	Fe.
Alizarin	Maroon.	Dull orange-red.	Bright reddish-orange.	Dull bluish-maroon.
Benzalizarin ...	Browner maroon.	Dull reddish-orange.	Bright orange.	Brownish-black.

The methylation of benzalizarin by means of methyl iodide and alkali was now studied in the hope that insight would thus be gained as to the exact position of its hydroxyl groups. Although it was at one time considered that by the use of these reagents it was not possible to methylate an hydroxyl group in the ortho-position with respect to a carbonyl group, this, at least in the case of colouring matters of the xanthone and flavone types, has now been shown to be incorrect (T., 1913, **103**, 1632). On the other hand, there is no doubt that the carbonyl group does here exert

some steric hindrance, and in any case methylation of the hydroxyl group adjacent thereto is not effected except by using a considerable excess of iodide and alkali.

A mixture of benzalizarin (2 grams), methyl alcohol (30 c.c.), and methyl iodide (12 c.c.) was heated to boiling, and a solution of 2·5 grams of potassium hydroxide in methyl alcohol added drop by drop during some hours. Crystals, evidently of the monomethyl ether, soon separated, but these dissolved as the operation proceeded. After two days, the excess of methyl iodide was removed, and the crystals which separated were collected, washed with water, and recrystallised from acetone, employing animal charcoal.

Found: C = 78·5; H = 4·7; Me = 10·1.

$C_{17}H_8O(OMe)_2$ requires C = 78·62; H = 4·82; Me = 10·30 per cent.

It was found necessary to carry out the Zeisel determination in two stages (*a* and *b*), owing to the fact that the demethylated benzalizarin, even in the presence of acetic anhydride, separated as a spongy, colloidal mass, and enveloped a certain amount of unattacked or partly attacked substance. Thus, after two and a-half hours' digestion, methyl iodide ceased to be evolved, and the product, washed with sulphurous acid, dried, and ground, was again submitted to the action of hydriodic acid.

Found: (*a*) Me = 9·13; (*b*) Me = 0·97 per cent.

The regenerated benzalizarin, when acetylated, gave the acetyl compound, melting at 199—201°.

In this first experiment, although obviously an excess of alkali was employed, the reaction appeared to be at an end when less than half the amount had been added, and a second trial was now carried out in the same way, but using a solution of only 1 gram of commercial stick potassium hydroxide* in methyl alcohol. The product, isolated as in the former instance, weighed 2·02 grams, and only a trace of partly methylated substance soluble in alkali was present.

Dimethoxybenzanthrone crystallises from acetone in yellow needles melting at 139—141°, and is soluble in sulphuric acid with an orange-red colour devoid of fluorescence. It readily yields oxonium salts, and of these the *sulphate*, which crystallises in scarlet needles, was not analysed, owing to lack of material.

The *platinichloride* separates from acetic acid in small, red, glistening prisms.

Found: Pt = 19·91.

$(C_{19}H_{14}O_3)_2H_2PtCl_6$ requires Pt = 19·70 per cent.

* The theoretical amount of pure potassium hydroxide required was 0·85 gram.

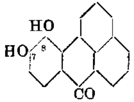
The *ferrichloride* consists of glistening, red needles.

Found: $C_{19}H_{14}O_3 = 74 \cdot 34$.

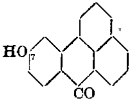
$(C_{19}H_{14}O_3)_2HFeCl_4$ requires $C_{19}H_{14}O_3 = 74 \cdot 45$ per cent.

For the sake of comparison with benzalizarin, alizarin itself was submitted to the action of methyl iodide under similar conditions to those given above, with the result that, as was to be anticipated, little or no methylation occurred, only a small amount of monomethyl ether being thus produced.

There is, accordingly, considerable difference between the behaviour of these two colouring matters in this respect, and there is strong probability, therefore, that as benzalizarin can be so readily methylated with methyl iodide, it cannot contain an hydroxyl group in the ortho-position with respect to the carbonyl. It will thus have the constitution (I), and from this the position of the hydroxy-group in the hydroxybenzanthrone (II) discussed in this paper will naturally follow.

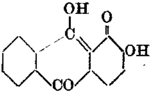


(I.)

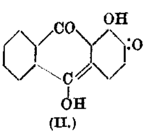


(II.)

Such being the case, it is very interesting that the dyeing properties of benzalizarin should so closely resemble those of alizarin. The latter are assumed to result from its possession of two hydroxyl groups in the ortho-position relatively to one another, one of which is adjacent to a carbonyl group. Based on this view, an ortho-quinonoid structure (I) for the alizarin lakes has been proposed (T., 1899, **75**, 433), but in case the constitution of benzalizarin given above receives full support, a para-quinonoid form (II) would prove more applicable.



(I.)

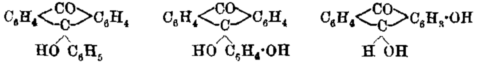


(II.)

The latter has, indeed, been previously suggested for the blue alkali salts of this colouring matter. The fact that benzanthrone and its hydroxy-derivatives give salts of an intensely coloured nature is interesting, in that, as these are presumably oxonium

compounds, their formation can only originate from the oxygen of the carbonyl group. Such a reaction is more usually associated with substances containing pyrone and analogous nuclei, and in these instances it is usually assumed that it is the basicity of the pyrone oxygen that comes into play. Salts of this character do not, for instance, appear to be producible from acetophenone, benzophenone, or their hydroxy-derivatives. On the other hand, when the carbonyl group forms part of a six-membered ring, as in benzanthrone, there is apparently further evidence that its basicity is thus increased. Thus, in case solution of a compound of this nature in sulphuric acid is accompanied by an intense colour, and addition of water precipitates the unchanged substance, it is reasonable to suspect the formation of an oxonium salt.*

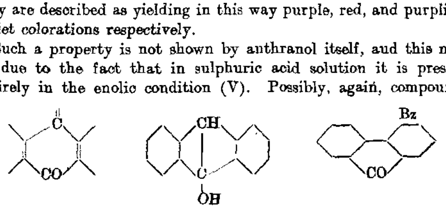
Whether the latter condition is fulfilled in all the substances here cited is, however, uncertain, but presuming this to be so, three compounds described by Baeyer, namely, phenylhydroxyanthranol (I), hydroxyphenylhydroxyanthranol (II), and phenolphthalidin (III) (*Annalen*, 1880, **202**, 58), which contain a nucleus



(I.) (II.) (III.)

(IV) similar to that present in benzanthrone, are interesting, as they are described as yielding in this way purple, red, and purplish-violet colorations respectively.

Such a property is not shown by anthranol itself, and this may be due to the fact that in sulphuric acid solution it is present entirely in the enolic condition (V). Possibly, again, compounds



(IV.) (V.) (VI.)

containing the carbonyl group in a five-membered ring may be reactive, for benzoylfluorenone (VI) (Götz, *Monatsh.*, 1902, **23**, 30) dissolves in sulphuric acid with a reddish-yellow tint.

Such colour changes are also given by compounds in which the carbonyl group is present in an open chain and adjacent to an unsaturated linking, and is, indeed, the property of numerous

* *It is singular, however, that the hydrocarbon carotene,* $C_{26}H_{38}$, dissolves in sulphuric acid with an indigo-blue coloration.

styryl methyl ketone (chalkone) derivatives. Moreover, oxonium salt-formation in the case of styryl methyl ketone,

$$CH_3 \cdot CO \cdot CH{:}CHPh,$$

itself seems certain, in that Baeyer and Villiger (*Ber.*, 1901, **34**, 2695) obtained therefrom the platinichloride,

$$(C_{10}H_{10}O)_2H_2PtCl_6,2H_2O,$$

in the form of yellow prisms. Curcumin (I), again, as is well

$$CH_2 < \begin{matrix} CO \cdot CH{:}CH \cdot C_6H_3(OH) \cdot OMe \\ CO \cdot CH{:}CH \cdot C_6H_3(OH) \cdot OMe \end{matrix} \qquad C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > C{:}CHPh$$

(I.) (II.)

known, dissolves in sulphuric acid with an intense red tint, whereas colour changes of this character are also given by certain derivatives of *benzylideneindandione* (II). *An investigation is in progress* with the object of obtaining more definite information as to the formation of oxonium salts in the case of these and allied compounds.

In connexion, again, with the present investigation, experiments were carried out to determine whether compounds of this character could be prepared from alizarin dimethyl ether, but, employing acetic acid for this purpose, no evidence of oxonium salt-formation could be observed either with mineral acids or anhydrous metallic compounds. On the other hand, it has been found that if rufigallol is stirred into concentrated sulphuric acid, maroon-coloured glistening, prismatic needles soon appear, which evidently consist of a sulphate. These may be collected on glass wool, but all attempts to remove adherent sulphuric acid without simultaneously dissociating the substance have hitherto been unsuccessful. Glacial acetic acid alone or admixed with acetic anhydride rapidly causes the production of bright red rufigallol, and even sulphuryl chloride gradually effects the same colour-change. It seems possible, however, that rufigallol methyl ether may furnish compounds of this character sufficiently stable for analysis, and experiments on this point are about to be undertaken.

Anthraquinone-1-carboxylic Acid.

As benzanthrone appeared to be a useful source of this acid for laboratory purposes, experiments were carried out in order to ascertain the best conditions for this purpose, and the following method was adopted.

A solution of 2 grams of benzanthrone in 20 c.c. of boiling acetic acid was slowly treated during three hours with a solution of 10 grams of commercial chromic acid in 20 c.c. of 50 per cent. acetic acid. The product, when diluted with hot water, deposited

crystals, and, after keeping overnight, these were collected. The filtrate, which contained some quantity of the anthraquinonecarboxylic acid in solution, was treated with sufficient sulphuric acid to convert the chromium into sulphate, evaporated to dryness, the residue extracted with water, and the crystals were collected. 2·091 Grams of the substance were thus isolated, which, however, contained chromium, and this was removed by treatment with 5 c.c. of sulphuric acid at 100° and subsequent precipitation with water. The product was dissolved in boiling dilute ammonia and the solution filtered, when, on acidification, the carboxylic acid was obtained in almost colourless needles melting at 286—288°, and weighing 1·8320 grams (Found: C=71·47; H=3·35. $C_{15}H_8O_4$ requires C=71·43; H=3·17 per cent.).

By recrystallisation from ten times its weight of nitric acid (D 1·42), and diluting the product with a little water, the preparation, which thus lost approximately 5 per cent. of its weight, melted at 291—292°.

Note on a Product of the Destructive Distillation of Sodium Anthraquinone-β-sulphonate.

Many years ago it was shown (A. G. and W. H. Perkin, T., 1885, **47**, 679) that when sodium anthraquinone-β-sulphonate is destructively distilled, there is produced, in addition to some quantity of anthraquinone and 2-hydroxyanthraquinone, a small amount of an orange-coloured substance. To the latter the formula $C_{28}H_{14}O_6$ was then assigned, and from this, by progressive oxidation, two colourless compounds, represented as $C_{28}H_{14}O_7$ and $C_{14}H_6O_4$, could be obtained. A further investigation of this subject was contemplated from time to time, but for the lack of a suitable apparatus capable of dealing with a large amount of the sulphonate, this has until very recently remained in abeyance. Although originally unsuspected, it has been known for some time that the compound to which the formula $C_{28}H_{14}O_6$ was assigned contains a small amount of sulphur. As a consequence, there can be little doubt that its true formula is $C_{28}H_{14}O_4S$, and with this the carbon and hydrogen analyses given in the paper are in full agreement. It is likely that this substance is in reality a thiodianthraquinone, $(C_{14}H_7O_2)_2S$, and, should this be the case, the formulæ of its oxidation products will thus be $C_{28}H_{14}O_5S$ and $C_{28}H_{14}O_6S$, and their constitutions naturally follow. It is interesting to note that in its reaction with sulphuric acid and general properties the former compound closely resembles the thiodianthraquinone prepared by

the interaction of 2-chloroanthraquinone and 2-thiolanthraquinone (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 274357). The further examination of these compounds and the study of a similar product from sodium anthraquinone-α-sulphonate, are in progress.

This statement has appeared necessary on account of a brief allusion to these componnds in a paper by Scholl, Schwinger, and Dischendorfer (*Ber.*, 1919, **52**, [*B*], 2260), and the opinion, "Man .kann sogar in Zweifel sein ob sie einheitliche Verbindungen in Händen gehabt haben," there given.

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LXXV.—n-*Butyl Chloroformate and its Derivatives.*

By FREDERICK DANIEL CHATTAWAY and EDOUARD SAERENS.

n-*Butyl chloroformate*, $Cl·CO_2·C_4H_9$, is best prepared by passing carbonyl chloride into cooled *n*-butyl alcohol until the calculated increase in weight is reached, and fractionally distilling the product.

It is difficult to separate the chloroformate from the unchanged *n*-butyl alcohol, and the yield is not large, as in the repeated fractional distillations necessary a considerable amount reacts with the alcohol to form di-*n*-butyl carbonate. If the first fractionations are slow, a distillate is frequently obtained which contains only this and *n*-butyl chloride.

n-Butyl chloroformate is a colourless, mobile liquid of a sharp, but pleasant, odour; the vapour attacks the eyes. It boils at 137·8°/734·5 mm., and has D_4^{25} 1·074 and $n_D^{8·4}$ 1·417.

It is only slowly hydrolysed when heated with water, in which it appears to be insoluble:

0·2587 gave 0·2725 AgCl. Cl=26·05.

$C_5H_9O_2Cl$ requires Cl=25·97 per cent.

Di-*n*-butyl carbonate, $(C_4H_9)_2CO_3$, was originally prepared by Lieben and Rossi (*Annalen*, 1873, **165**, 112) by heating *n*-butyl iodide with silver carbonate. The quantity obtained was very small, as much Δ^a-butylene and di-*n*-butyl ether are produced in the reaction.

It is always formed in small amount during the fractionation in the preparation of *n*-butyl chloroformate, and is easily obtained in quantity by passing carbonyl chloride into hot *n*-butyl alcohol or

by boiling *n*-butyl chloroformate with about twice the equivalent amount of *n*-butyl alcohol, and fractionating to separate any unchanged alcohol and the *n*-butyl chloride formed. Di-*n*-butyl carbonate is a colourless, mobile liquid of a somewhat pleasant smell, which boils at 207°/745 mm.

When *n*-butyl chloroformate is heated with any alcohol, it gives the corresponding alkyl *n*-butyl carbonate. The isolation of these alkyl *n*-butyl carbonates in a pure state by fractional distillation is generally tedious, as both the dialkyl carbonate and di-*n*-butyl carbonate are formed as well as the mixed ester, otherwise their preparation offers no difficulty. To avoid so far as possible the actions by which these by-products are formed, it is best to add the equivalent amount of the alcohol to boiling *n*-butyl chloroformate.

Methyl n-*butyl carbonate*, $C_4H_9\cdot O\cdot CO\cdot OMe$, is a colourless, mobile liquid having a sweet smell, somewhat recalling that of amyl acetate; it boils at 150·5°/745 mm.:

0·2154 gave 0·4301 CO_2 and 0·1769 H_2O. C=54·46; H=9·19.
$C_6H_{12}O_3$ requires C=54·50; H=9·15 per cent.

Ethyl n-*butyl carbonate*, $C_4H_9\cdot O\cdot CO\cdot OEt$, is a colourless, mobile, sweet-smelling liquid, which boils at 168·5°/748 mm.:

0·1757 gave 0·3693 CO_2 and 0·1507 H_2O. C=57·32; H=9·60.
$C_7H_{14}O_3$ requires C=57·49; H=9·65 per cent.

n-*Propyl* n-*butyl carbonate*, $C_4H_9\cdot O\cdot CO\cdot O\cdot C_3H_7$, is a colourless, mobile liquid having a pleasant smell, and boils at 187·5°/755 mm.:

0·1688 gave 0·3703 CO_2 and 0·1517 H_2O. C=59·83; H=10·05.
$C_8H_{16}O_3$ requires C=59·95; H=10·07 per cent.

n-Butyl chloroformate reacts very readily and energetically with ammonia and with amines to form *n*-butyl carbamates. In the case of ammonia, it is sufficient to shake vigorously the chloroformate with concentrated aqueous ammonia. With the amines it is best to add an ethereal solution of the base mixed with an equivalent amount of pyridine to an ethereal solution of the equivalent quantity of *n*-butyl chloroformate. The *n*-butyl carbamates are, as a rule, colourless, well-crystallised compounds readily soluble in alcohol or other ordinary organic solvents.

n-*Butyl carbamate*, $C_4H_9\cdot O\cdot CO\cdot NH_2$, is very readily soluble in alcohol, and crystallises in long, colourless, flattened prisms, which melt at 54°:

0·1814 gave 0·3402 CO_2 and 0·1527 H_2O. C=51·14; H=9·42.
$C_5H_{11}O_2N$ requires C=51·24; H=9·47 per cent.

n-*Butyl phenylcarbamate*, $C_4H_9{\cdot}O{\cdot}CO{\cdot}NHPh$, crystallises in long, colourless, flattened prisms, which melt at 65·5°:

0·2543 gave 0·6381 CO_2 and 0·1740 H_2O. C = 68·43; H = 7·65.
$C_{11}H_{15}O_2N$ requires C = 68·35; H = 7·83 per cent.

n-*Butyl* o-*chlorophenylcarbamate*, $C_4H_9{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_4Cl$, is an oily liquid boiling at 235—240°/60 mm., which does not solidify on keeping or when cooled in a freezing mixture:

0·3513 gave 0·2160 AgCl. Cl = 15·21.
$C_{11}H_{14}O_2NCl$ requires Cl = 15·58 per cent.

n-*Butyl*-p-*chlorophenylcarbamate* crystallises in colourless, flattened, apparently rhombic, prisms, which melt at 72°:

0·2346 gave 0·1492 AgCl. Cl = 15·73.
$C_{11}H_{14}O_2NCl$ requires Cl = 15·58 per cent.

n-*Butyl 2:4-dichlorophenylcarbamate*, $C_4H_9{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_3Cl_2$, crystallises in colourless, very slender prisms, which melt at 48°:

0·2070 gave 0·2261 AgCl. Cl = 27·02.
$C_{11}H_{13}O_2NCl_2$ requires Cl = 27·06 per cent.

n-*Butyl 2:4:6-trichlorophenylcarbamate*,
$C_4H_9{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_2Cl_3$,
crystallises in slender, colourless prisms, which melt at 60°:

0·2236 gave 0·3252 AgCl. Cl = 35·98.
$C_{11}H_{12}O_2NCl_3$ requires Cl = 35·88 per cent.

n-*Butyl* m-*bromophenylcarbamate*, $C_4H_9{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br$, crystallises in colourless, transparent, four-sided rhombic plates melting at 37·5°:

0·2425 gave 0·1669 AgBr. Br = 29·29.
$C_{11}H_{14}O_2NBr$ requires Br = 29·38 per cent.

n-*Butyl* p-*bromophenylcarbamate* crystallises in compact, colourless, rhombic prisms, which melt at 67°:

0·2424 gave 0·1670 AgBr. Br = 29·32.
$C_{11}H_{14}O_2NBr$ requires Br = 29·38 per cent.

n-*Butyl 2:4-dibromophenylcarbamate*, $C_4H_9{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_3Br_2$, crystallises in very slender, silky, hair-like prisms, which melt at 61·5°:

0·2130 gave 0·2278 AgBr. Br = 45·51.
$C_{11}H_{13}O_2NBr_2$ requires Br = 45·54 per cent.

n-*Butyl 2-chloro-4-bromophenylcarbamate*,
$C_4H_9{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_3BrCl$,
crystallises in very slender, hair-like prisms, which melt at 52°:

0·1913 gave 0·2061 AgCl + AgBr. Calc.: 0·2066 AgCl + AgBr.

n-*Butyl* p-*iodophenylcarbamate*, $C_4H_9\cdot O\cdot CO\cdot NH\cdot C_6H_4I$, crystallises in long, colourless prisms, which melt at 72°:

0·3048 gave 0·2232 AgI. I=39·58.
$C_{11}H_{14}O_2NI$ requires I=39·78 per cent.

n-*Butyl* o-*tolylcarbamate*, $C_4H_9\cdot O\cdot CO\cdot NH\cdot C_6H_4Me$, crystallises in colourless, slender prisms, which melt at 45·5°:

0·2173 gave 0·5534 CO_2 and 0·1596 H_2O. C=69·45; H=8·22.
$C_{12}H_{17}O_2N$ requires C=69·51; H=8·27 per cent.

n-*Butyl* p-*tolylcarbamate* crystallises in stout, colourless prisms, which melt at 63°:

0·2345 gave 0·5983 CO_2 and 0·1722 H_2O. C=69·58; H=8·21.
$C_{12}H_{17}O_2N_2$ requires C=69·51; H=8·27 per cent.

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[*Received, May 19th, 1920.*]

LXXVI.—*Isomeric Phthalylhydrazides.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM TESH.

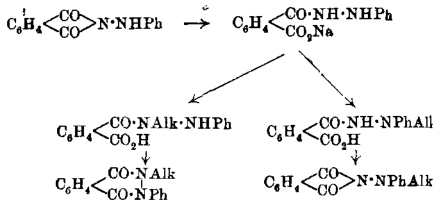
Two isomeric phthalylphenylhydrazides have been described, one yellow and crystallising in two enantiotropic modifications, the other colourless. The yellow compound has been much studied and the transition point of its polymorphs determined; its colourless isomeride has received less attention, and the conditions under which it is produced are still imperfectly understood. For convenience, the isomerides have been designated α- and β-phthalylphenylhydrazide, and the constitutions

$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot NHPh \qquad \text{and} \qquad C_6H_4{<}\begin{matrix}CO\cdot NH\\ \vert\\ CO\cdot NPh\end{matrix}$$

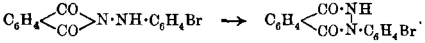
α-Phthalylphenylhydrazide (yellow). β-Phthalylphenylhydrazide (colourless).

have, with some justification, been assigned to them.

Pairs of isomerides similar in constitution and properties to these have been obtained by the action of alkyl iodides on the sodium salts of the phthalylhydrazinic acids, obtained by dissolving α-phthalylphenylhydrazide in an alcoholic solution of sodium ethoxide, for example:

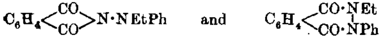


Although the α-phthalylhydrazides undergo no noticeable tran formation when heated in sealed tubes to temperatures below tho at which decomposition and gas evolution occur, those having hydrogen atom attached to the nitrogen atom carrying the ar group are gradually transformed into the correspondi β-isomerides when heated to about 210° for some hours wi glycerol or when boiled for a similar period with the equivale amount of sodium ethoxide dissolved in alcohol, thus:



EXPERIMENTAL.

α- and β-Phthalylphenylethylhydrazides,



α-. β-.

α-Phthalylphenylhydrazide was dissolved in an alcoholic soluti of an equivalent amount of sodium ethoxide, rather more than a equivalent amount of ethyl iodide added, and the mixture heat in a sealed tube to 120° for twelve hours. A brown mass was pr duced, which was dissolved in alcohol, and steam passed throu to remove the solvent alcohol and an excess of ethyl iodide. T solid product remaining was dissolved in boiling alcohol, and, cooling, yellow crystals of *α-phthalylphenylethylhydrazi* separated. The filtrate was concentrated and cooled, wh *β-phthalylphenylethylhydrazide* crystallised in white needle Each was then several times recrystallised from alcohol.

The yellow α-compound dissolves readily in boiling alcohol, a crystallises in long, yellow, flattened prisms melting at 134°:

0·2337 gave 21 c.c. N_2 (moist) at 15·8° and 764·5 mm. N = 10·5

$C_{16}H_{14}O_2N_2$ requires N = 10·52 per cent.

The colourless β-compound is very readily soluble in boiling alcohol, and crystallises in colourless needles melting at 109°:

0·1979 gave 17·8 c.c. N_2 (moist) at 11·6° and 756 mm. N = 10·61.

The yellow α-phthalylphenylethylhydrazide was also prepared by heating an alcoholic solution of α-phthalylphenylhydrazide with an equivalent amount of ethyl iodide in the presence of an equivalent amount of zinc oxide. In this experiment, none of the colourless β-compound was formed.

To establish the constitution of the yellow α-form, phenylethylhydrazine was prepared from monoethylaniline, and an alcoholic solution heated with phthalic anhydride.

The α-phthalylphenylethylhydrazide prepared in this way was identical with the yellow compound melting at 134°.

The β-phthalylphenylethylhydrazide (m. p. 109°), prepared as above, is certainly identical with that obtained by Hötte (*J. pr. Chem.*, 1887, [ii], **35**, 265) by heating ethyl iodide with a solution of β-phthalylphenylhydrazide in alcoholic potassium hydroxide. He describes it as crystallising in white needles melting at 105—106°. We have always, however, found the compound to melt at a slightly higher temperature, namely, 109°.

α- *and* β-*Phthalylphenyl*-n-*propylhydrazides*,

$$C_6H_4<{CO \atop CO}>N\cdot NPr^{\alpha}Ph \quad \text{and} \quad C_6H_5<{CO\cdot NPr^{\alpha} \atop CO\cdot NPh}.$$

These compounds were prepared exactly as the ethyl compounds, by heating a slight excess of *n*-propyl iodide with a solution of phthalylphenylhydrazide in an alcoholic solution of sodium ethoxide for sixteen hours to 125—130°.

α-*Phthalylphenyl*-n-*propylhydrazide* is readily soluble in alcohol, and crystallises in bright yellow, small, irregular rhombs, which melt at 110°:

0·3126 gave 26·5 c.c. N_2 (moist) at 13·8° and 760 mm. N = 9·96.
$C_{17}H_{16}O_2N_2$ requires N = 10·0 per cent.

β-*Phthalylphenyl*-n-*propylhydrazide* dissolves readily in alcohol, and crystallises in long, slender, colourless, six-sided prisms, which melt at 75°:

0·2935 gave 25·2 c.c. N_2 (moist) at 11·6° and 750 mm. N = 10·15.

*a- and β-Phthalylphenyl*iso*propylhydrazides,*

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot NPr^{\beta}Ph \quad \text{and} \quad C_6H_5<\genfrac{}{}{0pt}{}{CO\cdot NPr^{\beta}}{CO\cdot NPh}.$$

These were obtained in a similar manner to the norma compounds.

*a-Phthalylphenyl*iso*propylhydrazide* is readily soluble in alcohol and crystallises in bright yellow, rhombic plates, which melt a 142°:

0·3161 gave 27·8 c.c. N_2 (moist) at 17·2° and 750 mm. N=10·07

$C_{17}H_{16}O_2N_2$ requires N=10·0 per cent.

*β-Phthalylphenyl*iso*propylhydrazide* dissolves readily in alcohol and crystallises in slender, colourless, four-sided prisms, which melt at 103°:

0·3176 gave 0·8510 CO_2 and 0·1657 H_2O. C=73·07; H=5·79.

0·2218 „ 19·4 c.c. N_2 (moist) at 17° and 752 mm. N=10·04

$C_{17}H_{16}O_2N_2$ requires C=72·81; H=5·75; N=10 per cent.

a- and β-Phthalylphenylallylhydrazides,

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot NPh\cdot C_3H_5 \quad \text{and} \quad C_6H_5<\genfrac{}{}{0pt}{}{CO\cdot N\cdot C_3H_5}{CO\cdot NPh}.$$

These were prepared in a similar manner to the previously described compounds, the action with the allyl iodide being especially vigorous, heating for half an hour only on the water-bath being required to complete it.

a-Phthalylphenylallylhydrazide is readily soluble in alcohol, and crystallises in bright yellow prisms, which melt at 142°:

0·3068 gave 26 c.c. N_2 (moist) at 10° and 747·5 mm. N=9·97

$C_{17}H_{14}O_2N_2$ requires N=10·07 per cent.

β-Phthalylphenylallylhydrazide dissolves very readily in alcohol and crystallises in slender, colourless prisms, which melt at 90°:

0·2162 gave 18 c.c. N_2 (moist) at 13° and 756 mm. N=9·79.

Phthalylphenyltrimethylenebishydrazide.

Ninety grams of phthalylphenylhydrazide were dissolved in a solution of 6 grams of sodium in 200 c.c. of alcohol, and heated with 40·4 grams of trimethylene bromide on a water-bath for six hours.

The sodium bromide which separated was filtered off, 4 grams of sodium dissolved in alcohol were added, and the mixture was again heated for two hours. On adding water, *phthalylphenyltri-*

methylenebishydrazide separated as a white solid. It was recrystallised from hot alcohol, in which it is readily soluble, and separated in long, colourless, slender prisms melting at 187°:

0·1017 gave 0·2703 CO_2 and 0·0439 H_2O. C=72·48; H=4·79.
0·1475 „ 13 c.c. N_2 (moist) at 8° and 760 mm. N=10·64.
$C_{31}H_{24}O_4N_4$ requires C=72·1; H=4·65; N=10·8 per cent.

The compound, from its behaviour, has probably the bis-β-constitution, $C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot N\cdot CH_2\cdot CH_2\cdot CH_2\cdot N\cdot CO}{CO\cdot NPh \qquad\qquad PhN\cdot CO}>C_6H_4$.

*β-Phthalyl-*p*-bromophenylhydrazide,* $C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot N\cdot C_6H_4Br}$.

α-Phthalyl-*p*-bromophenylhydrazide has already been obtained by the interaction of phthalic anhydride and *p*-bromophenylhydrazine at 100°. It crystallises from hot alcohol in bright yellow, monoclinic prisms, which melt at 206° (Chattaway and Wünsch, T., 1911, **99**, 2260).

This compound was transformed into the sodium salt of the β-isomeride by heating with the equivalent quantity of sodium ethoxide in alcoholic solution in a sealed tube to 100° for eight hours. On adding hydrochloric acid to the solution, the β-isomeride separated. It was recrystallised from hot alcohol, in which it is moderately easily soluble, and separated in fine, white needles melting at 252°:

0·1149 gave 0·2270 CO_2 and 0·0315 H_2O. C=53·00; H=3·04.
0·1206 „ 8·9 N_2 (moist) at 9° and 760 mm. N=8·87.
$C_{14}H_9O_2N_2Br$ requires C=53·0; H=2·84; N=8·83 per cent.

*α- and β-Phthalyl-*p*-bromophenylallylhydrazides,*

$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot N<\genfrac{}{}{0pt}{}{C_3H_5}{C_6H_4Br}$ and $C_6H_5<\genfrac{}{}{0pt}{}{CO\cdot N\cdot C_3H_5}{CO\cdot N\cdot C_6H_4Br}$.

These compounds were prepared similarly to the corresponding phenyl derivatives, by heating allyl iodide with α-phthalyl-*p*-bromophenylhydrazide dissolved in an equivalent amount of alcoholic sodium ethoxide on a water-bath for seven to eight hours.

*α-Phthalyl-*p*-bromophenylallylhydrazide* is readily soluble in hot alcohol, and crystallises in bright yellow, slender, four-sided prisms, which melt at 118°:

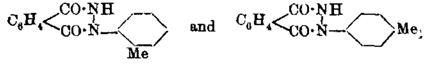
0·2893 gave 0·1453 AgBr. Br=21·37.
$C_{17}H_{13}O_2N_2Br$ requires Br=21·45 per cent.

*β-Phthalyl-*p*-bromophenylallylhydrazide* is moderately soluble in

hot alcohol, and crystallises in long, very thin, colourless needles melting at 129°:

0·0948 gave 0·0485 AgBr. Br = 21·71.

*β-Phthalyl-o-tolylhydrazide and β-Phthalyl-*p*-tolylhydrazide,*



a-Phthalyl-*o*-tolylhydrazide and *a*-phthalyl-*p*-tolylhydrazide have already been prepared by the interaction of phthalic anhydride and the corresponding tolylhydrazines; the former crystallises in small tabular, monoclinic, bright orange crystals, which melt at 198°, and the latter in long, deep orange, prismatic crystals, which melt at 196° (Chattaway and Wünsch, *loc. cit.*). They are both easily converted into the corresponding *β*-isomerides by heating in a sealed tube to 100° for eight hours with an alcoholic solution of the equivalent amount of sodium ethoxide, and precipitating by acid.

β-Phthalyl-o-tolylhydrazide is moderately readily soluble in hot alcohol, and separates in colourless, compact crystals, which melt at 207°:

0·2188 gave 20·8 c.c. N_2 (moist) at 13° and 751·5 mm. N = 11·10

$C_{15}H_{12}O_2N_2$ requires N = 11·11 per cent.

*β-Phthalyl-*p*-tolylhydrazide* dissolves moderately readily in hot alcohol, and crystallises in very slender, colourless prisms, which melt at 225°:

0·1438 gave 13·8 c.c. N_2 (moist) at 10° and 748 mm. N = 11·29

*a- and β-Phthalyl-*p*-tolylallylhydrazides,*

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot N<\begin{matrix}C_3H_5\\C_6H_4Me\end{matrix} \quad \text{and} \quad C_6H_4<\begin{matrix}CO\cdot N\cdot C_3H_5\\CO\cdot N\cdot C_6H_4Me\end{matrix}.$$

These were prepared similarly to the corresponding phenyl compounds.

*a-Phthalyl-*p*-tolylallylhydrazide* is very readily soluble in hot alcohol, and crystallises in bright yellow, irregular, rhombic plates which melt at 87°:

0·2095 gave 17·6 c.c. N_2 (moist) at 17° and 764 mm. N = 9·78.

$C_{18}H_{16}O_2N_2$ requires N = 9·6 per cent.

*β-Phthalyl-*p*-tolylallylhydrazide* is very readily soluble in hot alcohol, and crystallises in colourless, six-sided prisms, which melt at 102°:

[illegible]

Acyl Derivatives of the Phthalylhydrazides.

All the phthalylhydrazides containing hydrogen attached to nitrogen readily form colourless acyl derivatives. Several of these have been prepared from various members of the α- and β-series of hydrazides by heating them for some hours with formic acid, acetic, propionic or *n*-butyric anhydride, or benzoyl chloride in sealed tubes.

α-Phthalylformylphenylhydrazide, $C_8H_4O_2{:}N{\cdot}NPh{\cdot}CHO$, crystallises from alcohol in small, colourless rhombs melting at 185°:

0·2418 gave 21·8 c.c. N_2 (moist) at 16° and 759 mm. N = 10·48.

$C_{15}H_{10}O_3N_2$ requires N = 10·52 per cent.

α-Phthalylacetylphenylhydrazide, $C_8H_4O_2{:}N{\cdot}NPhAc$, crystallises from alcohol in colourless, flattened, four-sided prisms melting at 198°:

0·2035 gave 17·5 c.c. N_2 (moist) at 18° and 759 mm. N = 9·86.

$C_{16}H_{12}O_3N_2$ requires N = 10·0 per cent.

β-Phthalylacetylphenylhydrazide, $C_6H_4{<}\begin{matrix}CO{\cdot}NAc\\ CO{\cdot}NPh\end{matrix}$, crystallises from alcohol in colourless, prismatic crystals melting at 127°:

0·2256 gave 20·1 c.c. N_2 (moist) at 18° and 752 mm. N = 10·16.

$C_{16}H_{12}O_3N_2$ requires N = 10·0 per cent.

α-Phthalylpropionylphenylhydrazide, $C_8H_4O_2{:}N{\cdot}NPh{\cdot}COEt$, crystallises from alcohol in colourless, four-sided plates melting at 148°:

0·2481 gave 20·3 c.c. N_2 (moist) at 16° and 759 mm. N = 9·51.

$C_{17}H_{14}O_3N_2$ requires N = 9·52 per cent.

*α-Phthalyl-*n*-butyrylphenylhydrazide*, $C_8H_4O_2{:}N{\cdot}NPh{\cdot}CO{\cdot}C_3H_7$, crystallises from alcohol in short, white prisms melting at 126°:

0·2312 gave 17·8 c.c. N_2 (moist) at 17° and 748 mm. N = 8·78.

$C_{18}H_{16}O_3N_2$ requires N = 9·09 per cent.

*α-Phthalylformyl-*p*-bromophenylhydrazide*,

$C_8H_4O_2{:}N{\cdot}N(C_6H_4Br){\cdot}CHO$,

crystallises from alcohol in colourless, six-sided prisms melting at 176°:

0·2792 gave 0·1536 AgBr. Br = 23·4.

$C_{15}H_9O_3N_2Br$ requires Br = 23·2 per cent.

*α-Phthalylacetyl-*p*-bromophenylhydrazide*,

$C_8H_4O_2{:}N{\cdot}NAc{\cdot}C_6H_4Br$,

crystallises from alcohol in colourless prisms melting at 166°:

0·1763 gave 0·0914 AgBr. Br = 22·06.

$C_{16}H_4O_3N_2Br$ requires Br = 22·28 per cent.

*a-Phthalylbenzoyl-*p*-bromophenylhydrazide,*

$C_8H_4O_2\colon N\cdot NBz\cdot C_6H_4Br$,

crystallises from alcohol in colourless, small rhombs melting at 166°:

0·2032 gave 0·0920 AgBr. Br = 19·27.

$C_{21}H_{13}O_3N_2Br$ requires 19·0 per cent.

a-Phthalylformyl-o-tolylhydrazide, $C_8H_4O_2\colon N\cdot N(C_6H_4Me)\cdot CHO$, crystallises from alcohol in colourless, long, slender needles melting at 112°:

0·1472 gave 12·5 c.c. N_2 (moist) at 10° and 754 mm. N = 10·0.

$C_{16}H_{12}O_3N_2$ requires N = 10·0 per cent.

a-Phthalylacetyl-o-tolylhydrazide, $C_8H_4O_2\colon N\cdot NAc\cdot C_6H_4Me$, crystallises from alcohol in colourless, four-sided prisms melting at 161°:

0·2339 gave 19·3 c.c. N_2 (moist) at 18° and 759 mm. N = 9·51.

$C_{17}H_{14}O_3N_2$ requires N = 9·52 per cent.

a-Phthalylbenzoyl-o-tolylhydrazide, $C_8H_4O_2\colon N\cdot NBz\cdot C_6H_4Me$, crystallises from alcohol in colourless, stout, rhombic prisms melting at 151°:

0·2392 gave 16·2 c.c. N_2 (moist) at 17° and 760 mm. N = 7·85.

$C_{22}H_{16}O_3N_2$ requires N = 7·87 per cent.

*a-Phthalylformyl-*p*-tolylhydrazide* crystallises from alcohol in long, colourless prisms melting at 180°:

0·1776 gave 15·4 c.c. N_2 (moist) at 18° and 759·5 mm. N = 9·99.

$C_{16}H_{12}O_3N_2$ requires N = 10·0 per cent.

*a-Phthalylacetyl-*p*-tolylhydrazide* crystallises from alcohol in colourless, four-sided prisms melting at 151°:

0·1872 gave 15·2 c.c. N_2 (moist) at 17° and 759 mm. N = 9·4.

$C_{17}H_{14}O_3N_2$ requires N = 9·52 per cent.

*a-Phthalylbenzoyl-*p*-tolylhydrazide* crystallises from alcohol in colourless prisms melting at 135°:

0·1255 gave 8·4 c.c. N_2 (moist) at 10° and 752 mm. N = 7·92.

$C_{22}H_{16}O_3N_2$ requires N = 7·87 per cent.

Transformation of a- into β-Phthalylphenylhydrazide.

Although when the phenylhydrazinic acid formed by the combination of phenylhydrazine with phthalic anhydride loses water, the coupling probably takes place in two directions, leading to the production of the a- and of the β-isomeride, the amount of the latter formed at temperatures between 100° and 170° is so small as to be unrecognisable.

The decomposition of the α-compound into phthalanil, nitrogen, nd ammonia (compare Chattaway, Cumming, and Wilsdon, T., 911, **99**, 1951), which becomes vigorous at temperatures above 00°, takes place to a small extent at the lower temperature also, nd it is very difficult to separate the constituents of the small, iscid residue left on evaporating the mother liquor from which ie α-phthalylphenylhydrazide has crystallised.

That neither α- nor β-phthalylphenylhydrazide is transformed ppreciably into the other when heated alone was shown by heat-ig a few grams of each in sealed tubes to 250° for six hours. 'n once crystallising the solidified mass, the original compound 'as obtained in a pure state.

'ransformation of α- into β-Phthalylphenylhydrazide by Heating with an Alcoholic Solution of Sodium Ethoxide.

Sodium (2·3 grams) was dissolved in 100 c.c. of alcohol, 23·8 rams of α-phthalylphenylhydrazide were added, and the whole as heated on a water-bath for seven hours. After dilution with 'ater, the filtered liquid was acidified with hydrochloric acid, and ie white substance which separated was recrystallised from alcohol. t separated in colourless, compact, irregular crystals, which melted t 211—212° (Found: C=70·65; H=4·40; N=11·50. $C_{14}H_{10}O_2N_2$ equires C=70·59; H=4·20; N=11·77 per cent.). The substance, ierefore, is the β-phthalylphenylhydrazide described by Pellizzari *Gazzetta*, 1886, **16**, 200).

A number of similar experiments, in which portions of the boil-ig alcoholic sodium ethoxide solution were withdrawn from time › time and precipitated by hydrochloric acid, showed that at first ily phthalylphenylhydrazinic acid is obtained, β-phthalylphenyl-ydrazide slowly making its appearance, and increasing in amount ntil, after about five to six hours' heating, it alone is present.

ransformation of α- into β-Phthalylphenylhydrazide by Heating with Glycerol.

α-Phthalylphenylhydrazide was heated with about four times its eight of glycerol in an open tube for ten hours to 240°. On ooling, the mass was ground with water and well washed to emove the glycerol. The colourless solid remaining was dissolved . a cold dilute solution of potassium hydroxide, the liquid filtered id acidified with hydrochloric acid, and the white solid separating ice crystallised from alcohol.

It melted at 210°, and when mixed with β-phthalylphenylhydr-

azide, prepared from the α-hydrazide and sodium ethoxide, th melting point remained unaltered (Found: C=70·2; H=4·47 N=11·40. Calc.: C=70·59; H=4·20; N=11·77 per cent.) Similar experiments were made in which the time of heating wa varied. These showed that the transformation takes place slowly about 50 per cent. being transformed in from five to six hours.

On similarly heating α-phthalylphenylethylhydrazide wit glycerol, no change occurred, the original α-compound crystallisin out unaltered from a solution of the product in boiling alcoho and no other substance separated on evaporation of the filtrate.

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LXXVII.—*The Acylation of Thiocarbamides.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

IT has frequently been observed that the *N*-acylation of thiocarl amide is preceded by the fixation of the acyl radicle to the sulphu atom of the latter (Dixon and Hawthorne, T., 1907, **91**, 12 145; Dixon and Taylor, *ibid.*, 914; 1908, **93**, 29; 1912, **101**, 251 *et seq.*; Dixon and Kennedy, this vol., 81), a phenomenon th mechanism of which may be represented by the typical scheme:

$$\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!CS + AcX \longrightarrow \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C{:}S\!<\!\begin{matrix}Ac\\X\end{matrix} \longrightarrow$$
$$\text{(I.)}$$
$$\begin{matrix}NH_2\\NH\end{matrix}\!\!>\!C{\cdot}SAc \longrightarrow NH_2{\cdot}CS{\cdot}NHA$$
$$\text{(II.)} \qquad\qquad \text{(III.)}$$

On the other hand, in many cases no evidence is yet forthcomin that would justify such a view, the process apparently being accon plished through direct attack of the nitrogen. This, it no appears, is due sometimes (and possibly always) to the instabilit of the sulphonium salt (I) in the circumstances of its formation.

All such salts are readily dissociable by heat, with the eliminatio of HX, whence it follows that if a high temperature is essential t reaction, they are not likely to be discoverable in the produc Neither is the ψ-base (II), compounds of this class being alwa rather unstable. Moreover, a sulphonium salt, although initiall formed, may decompose, even in the cold; if so, a substance of ty (III) will constitute the actual product, both the others possib

escaping detection; in either case, *N*-acylation will seem to have occurred directly.

The acetylation of thiocarbamide by means of acetic anhydride is a case in point, heat being employed in the process (Nencki, *Ber.*, 1873, **6**, 599). As a matter of fact, reaction occurs spontaneously at the ordinary temperature; the change, however, requires several days for its completion, and at no stage is there a detectable amount of any transition product. Thiocarbamide–acetyl acetate is evidently very unstable: a suspension of thiocarbamide–acetyl iodide in cold acetone, when treated with sodium acetate, rapidly became clear, owing to the formation of sodium iodide, yet from the solution the salt, $\frac{NH_2}{NH_2}\!>\!C\!:\!S\!<\!\frac{COMe}{O\cdot COMe}$, could not be isolated, the product being merely acetylthiocarbamide.

Nevertheless, that the salt is capable of temporary existence may be inferred from another observation. Thiocarbamide and acetyl picrate, both in glacial acetic acid solution, show no tendency to unite, even after some days' keeping, but when acetic anhydride is added to the mixture, a deposition of thiocarbamide–acetyl picrate soon commences, the reaction within a few hours being complete. The acetyl picrate, therefore, although it fails to unite with the thiocarbamide, reacts with some material produced from the latter by the anhydride, capturing it at once, and thus precluding its normal change into acetylthiocarbamide. Manifestly that material is either thiocarbamide–acetyl acetate or the corresponding ψ-base (acetyl picrate does not combine with acetylthiocarbamide, and, if it did, the product would not be thiocarbamide–acetyl picrate).

When, instead of acetic acid, dry acetone is used as solvent, the same phenomena occur; but the yellow precipitate, if kept in contact with the liquor, presently redissolves, and later, acetylthiocarbamide is deposited. Thiocarbamide–acetyl picrate, therefore although producible in contact with acetone, gradually surrenders to it the elements of the conjoined picric acid, whereupon, as usual the acetyl group of the resultant ψ-base migrates from sulphur to nitrogen. The analogy between the result just mentioned and the foregoing results with (*a*) thiocarbamide and acetic anhydride and (*b*) thiocarbamide–acetyl iodide and sodium acetate, requires no comment.

Observing the production of "diacetylthiocarbamide" from thiocarbamide and acetic anhydride at 130° to be facilitated by the passage of hydrogen chloride into the mixture, E. A. Werner concludes (T., 1916, **109**, 1128) that the acid transforms the acetylthiocarbamide into a ψ-configuration, MeCO·NH·C(:NH)·SH

assumed to be more susceptible of attack by the anhydride. It is far from certain, however, that the hydrogen chloride acts solely on the acetylthiocarbamide, for, at a temperature much lower than 130°, it converts acetic anhydride freely into acetyl chloride, a more active substance than the anhydride. However that may be, the fact is that, in promoting the reaction, acetyl chloride serves just as effectively as hydrogen chloride.

The constitution, MeCO·NH·C(:NH)·S·COMe, proposed by him for "diacetylthiocarbamide" being apparently open to doubt, attempts were made to learn whether the acetylbutyryl derivative (from acetylthiocarbamide and butyryl chloride on the one hand, and from butyrylthiocarbamide and acetyl chloride on the other) could exist in two isomeric forms. The experiments were unsuccessful, as were similar ones in which it was sought to produce acetylbenzoyl derivatives.

iso*Thiohydantoins.*

As regards the behaviour of (say) chloroacetic acid (Rây and Fernandes, T., 1914, **105**, 2160) or of its esters (Taylor, this vol., p. 4) towards thiocarbamide, there is no reason to doubt the essential simplicity of the mechanism, represented by the scheme:

$$\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C{:}S\!<\!\!\begin{matrix}CH_2\cdot CO_2R\\Cl\end{matrix} \rightarrow \begin{matrix}NH_2\\NH\end{matrix}\!\!\geqslant\!C\cdot S\cdot CH_2\cdot CO_2R \rightarrow$$

$$NH{:}C\!<\!\!\begin{matrix}NH\cdot CO\\ \vert \\ S\!-\!\!-CH_2\end{matrix}.$$

Much less simple is the mechanism when (say) chloroacetyl chloride is caused to react with thiocarbamide or with its mono- or di-substitution derivatives, whereby, too, *iso*thiohydantoins are produced (Dixon and Taylor, T., 1912, **101**, 570). That is, the *collocation*, $\cdot S\cdot CH_2\cdot CO\cdot$, *becomes developed*, a *result that would be* intelligible if the components could yield initially the additive substance, $\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C{:}S\!<\!\!\begin{matrix}CH_2\cdot COCl\\Cl\end{matrix}$. Hitherto, indeed, changes of the kind have been represented as occurring on lines more or less consistent with such a view, and it is only of late that, by the authors at least, its inherent difficulties have been recognised.

For example, methylthiocarbanilide with chloroacetyl chloride yields, not $\begin{matrix}MePhN\\PhNH\end{matrix}\!\!>\!C{:}S\!<\!\!\begin{matrix}CH_2\cdot COCl\\Cl\end{matrix}$, but $\begin{matrix}MePhN\\PhNH\end{matrix}\!\!>\!C{:}S\!<\!\!\begin{matrix}CO\cdot CH_2Cl\\Cl\end{matrix}$ (Dixon and Taylor, T., 1912, **101**, 570), a result in keeping with the superior activity of the ·COCl fraction of the molecule. With chloroacetyl chloride, too, the speed of reaction is high, just as it is with acid chlorides in general, whereas, unless assisted by heat,

the reaction of a thiocarbamide with a halogenised acid or its ester is relatively very slow. On these grounds, one might expect the formation of *iso*thiohydantoin from thiocarbamide and chloroacetyl chloride (if it takes place on the lines previously supposed) to require at least some hours in the cold; further, by operating in the cold, one might hope, in that case, to isolate the presumable additive salt formulated above.

In practice, when bromoacetyl bromide was added to a solution of thiocarbamide in acetone, *iso*thiohydantoin hydrobromide was precipitated at once, a result tolerably decisive in showing that the fraction, $\cdot CH_2Br$, was not the primary agent in the change, but $\cdot COBr$ instead. If so, and notwithstanding that *iso*thiohydantoin had been generated, it remained now to be shown that the latter proceeded indirectly, from a compound, $\genfrac{}{}{0pt}{}{NH_2}{NH_2}\!\!>C\!:\!S\!<\!\genfrac{}{}{0pt}{}{CO\cdot CH_2Br}{Br}$. Ultimately, by operation with glacial acetic acid as solvent, that compound was isolated, chloroacetyl bromide in like circumstances furnishing $\genfrac{}{}{0pt}{}{NH_2}{NH_2}\!\!>C\!:\!S\!<\!\genfrac{}{}{0pt}{}{CO\cdot CH_2Cl}{Br}$. By dissolution in water, they *yielded thiocarbamide, hydrobromic acid, and bromo- or chloroacetic* acid respectively, but with alkali hydroxide afforded no *trace of α-thiolacetic acid, and hence contained no material including* the $\cdot S\cdot CH_2\cdot CO\cdot$ complex. As might have been expected, *however, they soon changed when kept in contact with acetone,* the respective products being *iso*thiohydantoin hydrobromide and *isothiohydantoin* hydrochloride.

Of these facts, the explanation, in the light of those acquired in *other researches, is now patent. From the additive salt, acetone* withdraws the halogen conjoined with sulphur, the product, a *ψ*-base, $NH_2\cdot C(:NH)\cdot S\cdot CO\cdot CH_2X$ (X = halogen), *changing*, by the usual migration of the acyl group, into $NH_2\cdot CS\cdot NH\cdot CO\cdot CH_2X$. No *matter how formed, a compound* of such type (or, for a matter of that, even of the type $NH_2\cdot CS\cdot NH\cdot CH_2\cdot CH_2X$; see Gabriel, *Ber.*, 1889, **22**, 1148) *is incapable* of existence in ordinary circumstances, changing at once into a cyclic isomeride, the essential nucleus of which is $N\cdot C\!<\!\genfrac{}{}{0pt}{}{N\cdot C}{S-C}$ (Dixon, T., 1897, **71**, 621 *et seq.*). *On the principles now suggested, the explanation of this last* change is not far to seek, because, in a molecule such as

$$NH_2\cdot CS\cdot NH\cdot CO\cdot CH_2X,$$

the fractions, $\cdot CH_2\cdot$ and $\cdot X$, by uniting with the sulphur atom, could yield $NH_2\cdot C\!<\!\genfrac{}{}{0pt}{}{NH\cdot CO}{SX-CH_2}$, a formula which the authors take as best expressing the constitution of an *iso*thiohydantoin salt.

Why chloroacetyl chloride when heated with a suitable thiocarbamide yields an *iso*thiohydantoin is now clear, for the *sulphonium salt, initially formed*, since it loses haloid acid by mere contact with acetone, must very readily be dissociable by heat. How pyridine facilitates acylation in the cold (Dixon and Taylor, T., 1912, **101**, 2518) is equally clear: it removes from the sulphonium salt the elements of an acid, without hydrolysing the resultant acylated ψ-base.

ψ-Thiocarbamides.

From methyl-ψ-thiocarbamide and benzoyl chloride, in the presence of alkali hydroxide, Johnson and Jamieson (*Amer. Chem. J.*, 1906, **35**, 297) obtained the compound $(PhCO)_2N\cdot C(:NH)\cdot SMe$. On the other hand, in the absence of an alkali, benzyl-ψ-thiocarbamide, even with a large excess of acetyl chloride, yields only the additive compound, $CSN_2H_3\cdot CH_2Ph,MeCOCl$, from which, on the withdrawal of hydrogen chloride, there results a monoacylated derivative of the ψ-thiocarbamide. Whether the additive compound is $\begin{matrix}NH_2\\NH\end{matrix}\!\!>C\cdot SCl<\!\!\begin{matrix}CH_2Ph\\COMe\end{matrix}$ or (more likely)

$$\begin{matrix}NH_2\\MeCO\cdot NH\end{matrix}\!\!>C:S<\!\!\begin{matrix}CH_2Ph\\Cl\end{matrix}$$

matters little: in either case, the sulphur atom, by the absorption of a single molecule of the acid chloride, has become fully charged, and until a condition is established favourable to the elimination of hydrogen chloride, further acetylation is barred.

A case not here touched on, except incidentally, is the behaviour of acylating agents with thiocarbamides containing a well-marked electronegative group. In this connexion, owing to the difficulty with which the substances combine spontaneously (Dixon and Hawthorne, T., 1907, **91**, 141), little is yet known of the mechanism.

Thiocarbamides containing an NH_2-substituent (thiosemicarbazides) combine directly with acetyl chloride, yielding well-marked salts, from which, on the withdrawal of hydrogen chloride, *N*-acetyl derivatives are produced (McKee, T., 1915, **107**, 1133). In these, not only the acetyl radicle, but also a phenyl group, can migrate from one point to another within the molecule.

Experimental.

I. Thiocarbamide–acetyl chloride was dissolved in cold pyridine, the solution when acidified with dilute acetic acid

depositing acetylthiocarbamide. Heat, therefore, is not essential to the transformation, $\genfrac{}{}{0pt}{}{NH_2}{NH}{>}C{\cdot}S{\cdot}COMe \longrightarrow NH_2{\cdot}CS{\cdot}NH{\cdot}COMe$. By boiling for an hour with acetone, the same change is effected. Aniline behaves differently, heat being evolved, with the production of acetanilide, but ready-formed acetylthiocarbamide is *practically unaffected* by aniline, even on heating.

II. Finely sifted thiocarbamide was kept at the ordinary temperature in contact with excess of acetic anhydride. Gradually, the powder disappeared, its place being taken completely, after the lapse of a week, by large, transparent, rhombic prisms. Neither they nor the liquor in which they were formed yielded at any time a precipitate with aqueous picric acid; hence, neither thiocarbamide–acetyl acetate nor acetyl-ψ-thiocarbamide was present in quantity. The crystals consisted of almost pure acetylthiocarbamide (yield, 52 per cent. of the theoretical), and from the liquor, on concentration, a further amount of slightly impure material was obtained.

Acetylthiocarbamide with dilute acetic acid and sodium nitrite yields in one minute a scarcely perceptible trace of thiocyanic acid; in like circumstances, thiocarbamide (compare Werner, T., 1912, **101**, 2183) gives a well-marked reaction in less than thirty seconds.

III. From thiocarbamide dissolved in acetone and acetyl iodide, crystals of the additive salt, $\genfrac{}{}{0pt}{}{NH_2}{NH_2}{>}C{:}S{<}\genfrac{}{}{0pt}{}{COMe}{I}$, were deposited. It melted and decomposed at about 106°, and yielded a *picrate*, but was soon resolved by cold water into thiocarbamide, acetic acid, and hydriodic acid (total acid found = 13/14ths of that calculated).

A suspension of the salt in dry acetone, when treated with one molecular proportion of dry sodium acetate, rapidly became clear, sodium iodide passing into solution (sodium acetate is practically insoluble in acetone). The solution, which gave no precipitate with aqueous picric acid, and hence no longer contained thiocarbamide–acetyl iodide, was concentrated at a low temperature to expel most of the acetone; it now had the pungent odour of acetic acid, and presently yielded crystals of acetylthiocarbamide.

When the experiment was performed with thiocarbamide–acetyl chloride, instead of the iodide, scarcely any sign of interaction was perceptible in the cold. On heating, acetylthiocarbamide was produced, together with sodium chloride, a result not necessarily due, however, to reaction between the first-named material and the sodium acetate (see I).

IV. From a solution of thiocarbamide in acetone, on treatment with *iso*butyryl chloride, the additive salt, $\genfrac{}{}{0pt}{}{NH_2}{NH_2}\!>\!C{:}S\!<\!\genfrac{}{}{0pt}{}{CO.C_3H_7}{Cl}$, was precipitated in flattened, lustrous needles melting, with effervescence, at 115—117°, and yielding with aqueous picric acid a bright yellow *picrate*, hydrolysed by warming with water (Found: Cl=19·25. $C_5H_{11}ON_2ClS$ requires Cl=19·5 per cent.). By heating at 120—130° until effervescence ceased, and recrystallising the product from water, *iso*butyrylthiocarbamide was obtained in pearly leaflets melting at 111—112° (Found: S=21·92. Calc.: S=21·91 per cent.).

An attempt, by heating the latter with acetyl chloride and glacial acetic acid, to produce a derivative containing both acetyl and *iso*butyryl was unsuccessful; neither did acetylthiocarbamide when heated with *iso*butyryl chloride yield the expected diacyl compound.

V. Acetylthiocarbamide when heated under reflux with benzoyl chloride in the presence of glacial acetic acid in a bath at 130—150° gave a solid, from which chloroform extracted a crystalline, yellow substance melting at 105°, and consisting, apparently, of the acetylbenzoyl derivative (Found: S=14·4. Calc.: S=14·42 per cent.). From benzoylthiocarbamide, however, similarly heated with acetyl chloride and acetic anhydride, nothing was obtained except benzoic acid and diacetylthiocarbamide.

VI. Into acetic anhydride at 115° excess of hydrogen chloride was passed, the solution, when distilled, yielding acetyl chloride in quantity. When the experiment was repeated, at 130°, with thiocarbamide in solution, the phenomena described by Werner (T., 1916, **109**, 1128) were verified, the product being a diacetyl derivative.

VII. Acetyl chloride was substituted for hydrogen chloride in an experiment similar to the last, the phenomena being visually the same as before, and from the solution, after it had been concentrated in a vacuum over sodium hydroxide, the same diacetyl compound was obtained. A like result followed when acetyl chloride was heated for some time with a solution of acetylthiocarbamide in glacial acetic acid under reflux.

VIII. A solution of picric acid in acetic anhydride, when kept for a few hours in contact with finely powdered thiocarbamide, transformed the latter completely into thiocarbamide–acetyl picrate melting at 120° (Found: S=9·2. Calc.: S=9·21 per cent.).

Ready-formed acetyl picrate and thiocarbamide, each dissolved in glacial acetic acid, showed, after two days' keeping, no sign of

interaction. When acetic anhydride was added to the mixture, crystals of thiocarbamide–acetyl picrate began to separate in the course of an hour or so, and, after about seven hours, were collected, the filtrate remaining permanently clear.

IX. Bromoacetyl bromide, when added to a cold solution of thiocarbamide in acetone, yielded a sandy, white powder readily soluble in water, and giving all the reactions of *iso*thiohydantoin hydrobromide (Found: S=16·2; HBr=41·4. Calc.: S=16·24; HBr=41·11 per cent.).

X. The preceding experiment being repeated with glacial acetic acid as solvent, white needles of the additive *compound*,

$$\begin{matrix}NH_2\\NH_2\end{matrix}\!>\!C{:}S\!<\!\begin{matrix}CO\cdot CH_2Br\\Br\end{matrix},$$

were deposited, highly deliquescent and readily soluble in water. The very acid aqueous solution yielded with picric acid only a slight precipitate, but contained hydrobromic and bromoacetic acids, together with thiocarbamide. It gave no precipitate when neutralised, and, after short boiling with dilute alkali hydroxide, it did not give Andreasch's reaction (*Ber.*, 1879, **12**, 1385) for α-thiolacetic acid, and hence contained no detectable trace of *iso*thiohydantoin (Found: S=12·2. $C_3H_6ON_2Br_2S$ requires S=11·51 per cent. Total acid=39/40ths of that calculated).

The salt, when kept for an hour in contact with dry acetone, changed little in appearance, except that it became granular; the residual solid, now no longer deliquescent, gave all the usual reactions of *iso*thiohydantoin hydrobromide, including the formation of a *picrate*, not hydrolysed by heating with water, but reappearing when its solution was cooled.

XI. When the last experiment was repeated, but with chloroacetyl bromide, a similar additive *compound* was obtained in rosettes of white prisms, decomposing at 110—112° (Found: Br+Cl=49·5. $C_3H_6ON_2ClBrS$ requires Br+Cl=49·46 per cent.). By dissolution in water, it gave thiocarbamide, hydrobromic acid, and chloroacetic acid, but not instantaneously, for the solution, if mixed at once with picric acid, yielded a bright yellow *picrate*, hydrolysed by gently heating with water. On contact with dry acetone, the substance lost the elements of hydrogen bromide, the residual solid consisting mainly of *iso*thiohydantoin hydrochloride (a trace of hydrobromide was also present); consequently, the original salt had the configuration $\begin{matrix}NH_2\\NH_2\end{matrix}\!>\!C{:}S\!<\!\begin{matrix}CO\cdot CH_2Cl\\Br\end{matrix}$.

XII. To benzyl-ψ-thiocarbamide in acetone a large excess of acetyl chloride was added, the white precipitate at first formed dissolving as the addition was continued. On cooling, rosettes of

slender needles were deposited, melting and decomposing at 140—142°, and having the properties to be expected of an additive salt. Notwithstanding that a great excess of the chloride had been used, a single molecular proportion alone reacted, the product being $CSN_2H_8\cdot CH_2Ph,MeCOCl$ (Found: Cl = 14·7. $C_{10}H_{13}ON_2ClS$ requires Cl = 14·52 per cent.), and from it the monoacetyl base was liberated by means of calcium carbonate (Found: S = 15·6. $C_{10}H_{12}ON_2S$ requires S = 15·38 per cent.). It melted at 132°; but the same base, prepared from acetylthiocarbamide and benzyl chloride, shrank at 125° and melted at 128° (Found: S = 15·5).

The substance, presumably $NH_2\cdot C(:N\cdot COMe)\cdot S\cdot CH_2Ph$, was obtained in such poor yield (sometimes none at all) as to defeat projected experiments on its further possible combination with acetyl chloride.

CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE, CORK. [*Received, May 20th*, 1920.]

LXXVIII.—*A New Series of Nitrogenous Compounds obtained from Camphoroxalic Acid.*

By PERCY CHORLEY and ARTHUR LAPWORTH.

WHEN nitrous acid reacts with compounds containing the group $\cdot CO\cdot CHR\cdot CO\cdot$, the nitroso-compounds, $\cdot CO\cdot CR(NO)\cdot CO\cdot$, which are doubtless the initial products in all instances, tend to absorb the elements of water (or alcohol), with simultaneous severance of a "bond" between two of the carbon atoms in the second structure above depicted, yielding $\cdot CO_2H$ (or $\cdot CO_2Et$) and $\cdot CR(:NOH)\cdot CO\cdot$.

In the course of experiments which were instituted for the purpose of simplifying the methods at present available for converting ketones into their *iso*nitroso-derivatives, the action of nitrous acid on camphoroxalic acid was studied. It was anticipated that the nitroso-compound (I) of this substance would show complete analogy to the nitroso-derivatives of substituted malonic and acetoacetic acids, and become converted, with absorption of the elements of water, either into *iso*nitrosocamphor (II) and oxalic acid, or into the *iso*nitroso-acid (III).

$$C_8H_{14}<\begin{matrix}C(NO)\cdot CO\cdot CO_2H\\ CO\end{matrix} \quad C_8H_{14}<\begin{matrix}C:NOH\\ CO\end{matrix} \quad C_8H_{14}<\begin{matrix}C(:NOH)\cdot CO\cdot CO_2H\\ CO_2H\end{matrix}$$

(I.) (II.) (III.)

A transient blue colour, doubtless that of the nitroso-compound

(I), is observed when nitrous acid acts on camphoroxalic acid in aqueous solution. A small quantity of *iso*nitrosocamphor (II) is formed, but the main quantity of the nitroso-compound decomposes, with the elimination of carbon dioxide and the formation of a crystalline acid (A_1), $C_{11}H_{17}O_4N$, apparently in accordance with the equation

$$C_{12}H_{15}O_5N + H_2O = C_{11}H_{17}O_4N + CO_2.$$

The properties of the new acid are very difficult to reconcile with any quite straightforward assumptions as to its structure. It evinces remarkable stability towards both acids and alkalis; hot concentrated hydrochloric acid has no appreciable effect on it; boiling 50 per cent. aqueous potassium hydroxide, after prolonged contact, does not cause elimination of ammonia or hydroxylamine, but merely converts it into an isomeric acid (A_2), the properties of which so closely resemble those of the original compound as to leave little or no doubt that the isomerism is steric in character.

The most important properties of the acid (A_1) are the following:

(1) It is a monobasic acid with distinct amphoteric characters. (2) It reacts very readily with phosphorus pentachloride, and the product is at once converted by water into the original acid. (3) It yields camphoric acid when oxidised. (4) It is devoid of ketonic or aldehydic properties. (5) It is easily reduced by ferrous hydroxide in the presence of alkalis, although many of the ordinary reducing agents are without appreciable effect on it. (6) It gives an intense red coloration with aqueous ferric chloride.

The behaviour of the acid (A_1) on methylation is very significant. When methylated with methyl sulphate and alkali, it is converted into (*a*) a monomethyl "derivative" which is capable of expelling carbon dioxide from aqueous sodium carbonate, but gives no coloration with ferric chloride, and (*b*) a dimethyl "derivative" which is devoid of all acid properties, gives no coloration with ferric chloride.

The methyl groups in the dimethyl "derivative" are evidently both attached to oxygen, and not to nitrogen, for when this compound is hydrolysed by means of alkalis, the whole of its nitrogen is liberated in the form of ammonia, and no trace of methylamine can be detected. The coloration with ferric chloride which the original acid and its monomethyl "derivative" afford, indicates very clearly that in these two compounds there is present a grouping of the enol type, that is, $\dot{C}:C(OH)\cdot$ or $\cdot N:C(OH)\cdot$. On the other hand, the pronounced acidity of the acid and of its monomethyl "derivative" points to the presence in their molecules of

the free carboxyl group, a conclusion with which the behaviour of the acid towards phosphorus pentachloride is in entire agreement. The following formulæ serve to indicate the relation between the monomethyl "derivative" (IV), the true monomethyl ester, hitherto not isolated (V), and the dimethyl "derivative" (VI). The sign O^{en} is used to emphasise the conclusion that the oxygen atom is associated with doubly-bound carbon (enol type of structure).

$$MeO^{en}\cdot C_{10}H_{15}ON\cdot CO_2H \quad \text{(IV.)} \qquad HO^{en}\cdot C_{10}H_{15}ON\cdot CO_2Me \quad \text{(V.)}$$

$$MeO^{en}\cdot C_{10}H_{15}ON\cdot CO_2Me \quad \text{(VI.)}$$

The ease with which the acid (A_1) is reduced by meaus of ferrous hydroxide affords evidence that the nitrogen atom is directly attached to oxygen, but as the reactions of the compounds exclude the occurrence of the groups $>C{:}NOH$ and $\cdot\dot{C}\cdot NH\cdot OH$, it must be inferred that the complex $>N\cdot O\cdot$ is present as part of a ring. The ready response to alkaline ferrous hydroxide shown by certain *iso*oxazolones, which also have this structural peculiarity, has previously been noticed (T., 1907, **91**, 1919).

Whilst the original acid (A_1) is remarkably stable towards alkalis, the dimethyl derivative is readily hydrolysed by them, with evolution of ammonia and formation of a dibasic acid, $C_9H_{14}O(CO_2H)_2$, in accordance with the equation:

$$C_{11}H_{17}O_4N + H_2O = C_9H_{14}O(CO_2H)_2 + NH_3.$$

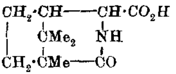
This substance has all the characters of an α-ketonic acid, and is readily oxidised by lead dioxide or manganese dioxide in aqueous solution. Its oxime when heated loses water and carbon dioxide, and is converted into α-camphornitrilic acid (IX), which observation decides the structure of the ketonic acid as (VII), and that of the oxime as (VIII).

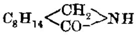
$$C_8H_{14}<^{CO\cdot CO_2H}_{CO_2H} \quad \text{(VII.)} \qquad C_8H_{14}<^{C(:NOH)\cdot CO_2H}_{CO_2H} \quad \text{(VIII.)} \qquad C_8H_{14}<^{CN}_{CO_2H} \quad \text{(IX.)}$$

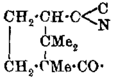
Additional light was thrown on the structure of the acid (A_1) by a study of the product which is obtained on reducing it with alkaline ferrous hydroxide. This product is a monobasic acid, $C_{11}H_{17}O_3N$, and is formed by the simple withdrawal of one atomic proportion of oxygen from the molecule of the parent acid. The new substance is extraordinarily stable towards powerful acids and alkaline hydrolytic agents, but its silver salt decomposes fairly

regularly in a stream of carbon dioxide, and the distillate consists almost wholly of *a*-camphidone (XI).

The properties of the monobasic acid are readily explained on the assumption that it is the monocarboxylic acid of *a*-camphidone (XI), and consideration of the relation of the present series of compounds to nitrosocamphoroxalic acid (I) and to *a-ketohomocamphoric acid* (VII) shows that the structure of the *camphidonecarboxylic acid* is represented by (X).

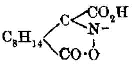

(X.)

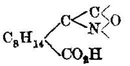

(XI.)

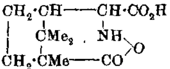

(XII.)

It has been already remarked that in the formation of the acid (A_1) from camphoroxalic acid, the nitroso-compound (I) represents an intermediate step. This, taken in conjunction with the conversion of A_1 into camphidonecarboxylic acid (X) on the one hand, and into *a*-ketohomocamphoric acid (VII) on the other, leaves no reasonable doubt that the acid (A_1) and its derivatives contain the structure (XII).

In order to satisfy the further conditions: (1) that the molecule includes the structure $\dot{N}\cdot O\cdot$ as part of a ring, and (2) that one carboxyl group is present, one of the two following skeleton structures must be selected as the framework of any structural formula for the acid (A_1):


(XIII.)


(XIV.)

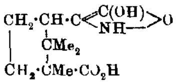

(XV.)

The only possible structural formula for a compound, $C_{11}H_{17}O_4N$, based on (XIII) is (XV).

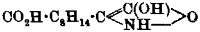
This is, however, wholly incompatible with the behaviour of the substance on methylation, as the lactonic carbonyl group would be attached to a quaternary carbon atom, and such a structure cannot be considered capable of existence in an enolic form without doing violence to all accepted canons. Formation of a dimethyl ester would necessitate the absorption of the elements of water, and this does not occur.

The authors, after very long consideration, have been forced to adopt (XIV) as the basis of a formula for the ultimate product obtained by the action of nitrous acid on camphoroxalic acid. On this basis, several "tautomeric" forms are possible for the acids

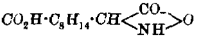
A_1 and A_2, and these, without introducing various other possibilities suggested by internal-salt formation, are as follows:



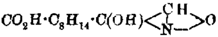
or



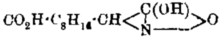
(XVI.) (XVI.)



(XVII.)



(XVIII.)



(XIX.)

Of these, probably (XVI) and its ketonic form (XVII) are much to be preferred, as (XVI) is the only one which contains the true enol grouping ·C(OH):C·, towards which the properties of the acids A_1 and A_2 significantly point. On the other hand, (XVIII) and (XIX) cannot yet finally be excluded, and they recall the structures which have long been adopted as the most satisfactory ones for anthranil, anthroxamic acid, and especially for the "oxyanthranil" or benz*iso*oxazolone of Bamberger and Pyman (*Ber.*, 1909, **42**, 2299).

In each of the above formulæ there is present a four-membered heterocyclic nucleus never previously identified in any compound, and until further instances of the structure come to light, the question of a suitable nomenclature for the present series of substances may be deferred.

It is worthy of note that the formation from the nitroso-compound (I) of a substance having any of the structures (XVI), (XVII), (XVIII), or (XIX) is associated with an engagement between the nitroso-group and the ketonic carbon atom in the complex, $\cdot CO\cdot CO_2H$. This renders it easy to understand what is otherwise incomprehensible, namely, why carbon dioxide should be eliminated during the formation of the acid (A_1), for the relations of the carbon atom to which the carbonyl group is attached are fundamentally altered by such an engagement. Such a consideration lends considerable weight to the more formal reasons which independently led the authors to reject (XV) and all other formulæ than those containing the four-membered rings.

The isomerism of the acids A_1 and A_2 is probably not such as exists, for example, between any two of the four alternative formulæ above given. It is more likely that both acids are ex-

relations of the atoms and groups about the four-membered ring. It is not impossible that the stereochemistry of the nitrogen atom is here involved.

The reduction of the acid (A_1) to α-camphidonecarboxylic acid by means of alkaline ferrous hydroxide is understood readily enough with the aid of formula (XVI) in association with the fact that this agent converts the group $>N\cdot O\cdot$, even when present as part of a ring, into $>NH$, if necessary with ring scission. Thus (XVI) becomes reduced to

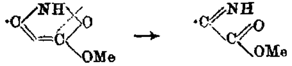
$$CO_2H\cdot C_8H_{14}\cdot CH<^{CO_2H}_{NH_2},$$

which would at once, on acidification, undergo conversion into its lactam, and the latter is nothing else than the α-camphidonecarboxylic acid (X) in question.

Adopting (XVI) for the acid A_1, the structure of the acid methyl "derivative" of this becomes

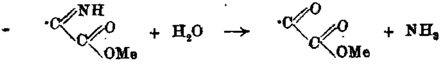
$$CO_2H\cdot C_8H_{14}\cdot C<^{C(OMe)}_{NH}>O.$$

The mechanism by which this substance yields ammonia, methyl alcohol, and α-ketohomocamphoric acid on treatment with alkali is somewhat obscure, but, as it involves the intramolecular reduction of an $>N\cdot O\cdot$ group, it is perhaps not distantly related to the "Beckmann change" of oximes. A simple rearrangement of the bonds in the four-membered ring of the above structure corresponds with such a reduction, and furnishes a new structure which obviously represents the imino-derivative (XX) of α-ketohomocamphoric methyl ester (XXI), which on hydrolysis would, of course, yield exactly the products actually observed.



and

(XX.)



(XX.)

EXPERIMENTAL.

Ethyl camphoroxalate was prepared by the action of sodium on a mixture of ethyl oxalate and camphor (compare Tingle, *Amer. Chem. J.*, 1897, **19**, 393), but in working up the product considerable improvements were effected by subjecting the crude

material to the action of a current of steam for about fifteen minutes. The latter treatment removes unaltered camphor with other volatile impurities, and the residual oil, collected and exposed over sulphuric acid in a vacuum for some hours, crystallises, if subsequently cooled in a freezing mixture, and then merely requires draining on porous earthenware before crystallisation from light petroleum.

To obtain camphoroxalic acid, the crude product, after treatment with steam, can with advantage be hydrolysed by leaving it in contact with 10 per cent. cold aqueous potassium hydroxide for three days. Subsequent addition of dilute sulphuric acid causes precipitation of camphoroxalic acid in a state sufficiently pure for most purposes.

Formation of the Acid A_1, $CO_2H{\cdot}C_8H_{14}{\cdot}C{<}^{C(OH)}_{NH}{>}O$.

Camphoroxalic acid (20 grams), dissolved in a 10 per cent. solution of aqueous sodium hydroxide (40 c.c.), is mixed with a 10 per cent. solution (63·8 c.c.) of sodium nitrite. Ten per cent. hydrochloric acid (100 c.c.) is then added very slowly below the surface of the liquid, when at first each small addition produces a white precipitate, which almost at once dissolves, forming an intensely green solution. This colour is not very fugitive at 10°, but at the ordinary temperature rapidly changes to yellow; it is not in any way due to free nitrous acid, as the solution does not react with starch–potassium iodide paper; the phenomena rather indicate the presence of a true nitroso-compound.

The continued addition of hydrochloric acid, which should occupy in all about ninety minutes, ultimately leads to the evolution of carbon dioxide and the separation of a brown oil, which contains free camphor, camphorquinone, and camphoroxalic acid. The aqueous liquor is separated from the oil and evaporated under diminished pressure nearly to dryness, during which process an appreciable quantity of camphorquinone at first passes over. The concentrated residue deposits a white solid when cool; the latter is removed, drained, extracted with ethyl acetate, and the extract filtered and cooled. A mass of white needles is then obtained, the quantity of which can be increased by further similar treatment of the filtrate, and the total yield approaches 77 per cent. of that theoretically possible.

The new substance is best purified by crystallisation from ethyl acetate, from which it reappears as a felted mass of needles. It dissolves freely in water, forming a strongly acid solution, and it is freely soluble also in alcohol, acetone, ethyl acetate, or chloro-

form; it is not freely dissolved by ether, and is insoluble in benzene or light petroleum.

Hydrochloric acid greatly increases the solubility of the compound, which therefore displays a basic as well as an acid character.

The crystals from ethyl acetate contain solvent of crystallisation, which, however, is rapidly lost on exposure to the atmosphere. A specimen left until constant in weight was analysed (Found: C=58·2; H=7·6; N=5·9. M.W.=230. $C_{11}H_{17}O_4N$ requires C=58·2; H=7·5; N=6·2 per cent. M.W.=227).

0·1605 Gram required 28·3 c.c. of 0·0248 *N*-NaOH for neutralisation, using phenolphthalein; equivalent=229. A monobasic acid, $C_{11}H_{17}O_4N$, has the equivalent 227.

0·6388 Gram dissolved and made up to 10 c.c. with absolute alcohol at 17° gave α_D 0·39° in a 1-dcm. tube, whence $[\alpha]_D^{17}$ 6·10°.

The pure compound melts at 160°, simultaneously evolving carbon dioxide and leaving a residue devoid of acid characters, but still more decidedly basic than the original substance. It is remarkably stable towards acids, and no change could be detected in it after prolonged boiling with saturated aqueous hydrochloric acid or after heating for six hours on the water-bath with concentrated sulphuric acid or aqueous hydrobromic acid. Hydrogen peroxide had no effect on it, but nitric acid oxidised it to camphoric acid with great facility. It is vigorously attacked by phosphorus pentachloride in dry ether, hydrogen chloride being copiously evolved; but the product, on treatment with ice-water, is at once converted into the original acid, and this suggests that the product in question is the normal carboxylic chloride.

The acid in aqueous solution gives an intense violet-red coloration with ferric chloride. It does not reduce Fehling's solution even after prolonged boiling with hydrochloric acid. No oxime, semicarbazone, or hydrazone could be prepared from it. Under certain conditions it reacts, in the presence of alkali, with toluenesulphonyl chloride, yielding an unstable, non-acidic oil, which dissolves in dilute hydrochloric acid; the true nature of this oil and the precise conditions necessary for its formation have not been determined.

The dilute solution of the sodium salt gives no precipitates with salts of silver, mercury, or barium, but with copper acetate it yields a bright green precipitate, which is soluble both in alcohol and chloroform; with lead acetate, a white salt is deposited unless the dilution is excessive.

Formation of the Isomeric Acid A_2, $CO_2H\cdot C_8H_{14}\cdot C{<}{\overset{C(OH)}{\underset{-NH-}{}}}{>}O$.

This is formed when the original acid (A_1) (10 grams) is boiled for twenty-four hours with a 50 per cent. solution of potassium hydroxide (100 c.c.). It is isolated by acidifying with hydrochloric acid and extracting with ether, and crystallises from ethyl acetate in colourless prisms, which are free from solvent of crystallisation (Found: C=57·9; H=7·6; N=6·2. $C_{11}H_{17}O_4N$ requires C=58·2; H=7·5; N=6·2 per cent.).

0·1738 Gram required 61·5 c.c. of 0·01240 *N*-NaOH for neutralisation, using phenolphthalein; equivalent=227. Calc., 228.

0·3809 Gram, dissolved and made up to 10 c.c. with absolute alcohol, gave α_D 0·99° at 17° in a 1-dcm. tube, whence $[\alpha]_D^{17}$ 25·99°.

The substance melts and decomposes at 205°, evolving carbon dioxide and leaving a basic residue; it closely resembles the isomeride in all essential chemical characters and in its behaviour towards solvents. In aqueous or alcoholic solution, it gives intense violet-red colorations with ferric chloride, and when dissolved in aqueous sodium hydrogen carbonate it instantly decolorises potassium permanganate. It is not appreciably hydrolysed by either hot aqueous alkalis or acids. The salts are freely soluble in water, with the exception of that of lead.

The acid behaves towards methyl sulphate and alkali in much the same manner as does the isomeride; no serious attempt has been made to purify the product, which is usually oily, but it was observed that it readily evolved ammonia when boiled with 50 per cent. potassium hydroxide. The similar behaviour of the isomeride in these circumstances is described later.

Thermal Decomposition of the Acid A_1.

When the original carboxylic acid is heated above its melting point, it evolves carbon dioxide and leaves a resinous mass. The product obtained by heating 90 grams of the acid at 160—170° for forty-five minutes dissolved completely in concentrated hydrochloric acid, but the solution, when diluted, deposited a considerable amount of tarry matter easily separated by filtration; the filtrate, rendered strongly alkaline with sodium hydroxide, yielded to ether 1·4 grams of a yellow base, freely soluble in the common oxygen-containing solvents, but sparingly so in benzene or petroleum. The base was obtained in fern-like plates, melting and decomposing at 232°, by extraction with boiling petroleum (b. p. 100—120°).

Analyses and molecular-weight determinations of different pre-

parations of the base gave numbers indicating the presence of a compound having the formula $C_{10}H_{17}O_2N$, but contaminated with 10—20 per cent. of another, $C_{10}H_{17}ON$ or $C_{10}H_{15}ON$, this suggesting that partial reduction or dehydration accompanies the elimination of carbon dioxide from the carboxylic acid; all attempts to separate the constituents of the mixture by fractional crystallisation before or after conversion into picrates were fruitless. The mixture gives no coloration with ferric chloride, and in many respects resembles α-camphidone, although the presence of the latter seemed improbable, as no characteristic picrate could be prepared from the material.

Methylation of the Acid A_1.

(*a*) *With the Silver Salt and Methyl Iodide.*—The silver salt was prepared by neutralising the aqueous solution of the acid with silver carbonate, evaporating to dryness, and heating the residue cautiously. It was then heated with methyl iodide in anhydrous ether for two hours. The filtered ethereal solution, evaporated to dryness, gave an oil, which, when washed with aqueous sodium hydrogen carbonate, was converted into a white solid, insoluble in water. This melted at about 230°, had no acidic properties, but gave an intense red coloration with ferric chloride in alcoholic solution. When boiled with water, it slowly dissolved, forming a solution which responded to the same tests as did the original carboxylic acid. The substance did not, however, respond to the tests for a methyl ester, and its nature remains uncertain, although analysis showed that the elements of carbon dioxide had been lost; it may be identical with one of the products obtained on heating the acid A_1.

(*b*) *With Alkali and Methyl Sulphate.*—The acid (18·5 grams) was dissolved in methyl alcohol (100 c.c.) containing methyl sulphate (24 grams). To this was then added gradually methyl alcohol (200 c.c.) containing potassium hydroxide (20 grams), and the whole allowed to remain during the night. The alcohol was then removed by evaporation and the residue dissolved in water, the resulting solution being extracted with ether. From the latter about 6 grams of a basic oil were obtained, whilst the residual aqueous liquor, when acidified with hydrochloric acid and again extracted with ether, yielded about 13 grams of a colourless acid.

The Monomethyl "Derivative," $CO_2H{\cdot}C_8H_{14}{\cdot}C{<}^{C(OMe)}_{-NH-}{>}O$.

The foregoing colourless acid was purified by crystallisation from acetone (Found: C = 59·4; H = 7·9; N = 6·0. $C_{12}H_{19}O_4N$ requires C = 59·7; H = 7·9; N = 5·8 per cent.).

The equivalent, determined by titration with sodium hydroxide, using phenolphthalein, was 232; Calc., 241. The substance separates from acetone in large, colourless octahedra, which melt and decompose slightly at 172°. It dissolves freely in alcohol, water, acetone, or ethyl acetate, less readily in ether or benzene, and is insoluble in cold light petroleum. Its aqueous solution gives no coloration with ferric chloride, but instantly decolorises permanganate and bromine water. When boiled with concentrated aqueous alkalis, it is decomposed, as described later.

If the silver salt of this acid is distilled in a vacuum, carbon dioxide is eliminated, and a basic solid distils. This solid is not homogeneous, but when fractionated by recrystallisation from petroleum (b. p. 60—70°) yields a crystalline material closely resembling impure α-camphidone; on recrystallisation of the picrate, a salt was isolated which had the same form as the picrate of α-camphidone, but the melting point was much too low, and the identity of the above solid remains somewhat doubtful.

The Dimethyl "Derivative" (Methyl Ester of the Monomethyl "Derivative"), $CO_2Me{\cdot}C_8H_{14}{\cdot}C{<}^{C(OMe)}_{-NH-}{>}O$.

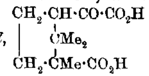
The basic substance obtained during the methylation of the hydroxycarboxylic acid was purified by crystallisation from dilute alcohol (Found: C = 60·9; H = 7·7. $C_{13}H_{21}O_4N$ requires C = 61·2; H = 8·2 per cent.).

This ester, although somewhat sparingly soluble in cold water, readily forms supersaturated solutions in it, and from these, on nucleation, it separates in slender needles, which in the course of a few days change into rhombic prisms melting at 115°. It dissolves freely in hot water, and also in ether, alcohol, acetone, or benzene, but only sparingly in petroleum.

In virtue of its basic character, the ester is freely soluble in weak or concentrated hydrochloric acid, and is reprecipitated on addition of alkali.

Action of Alkalis on the Methyl Derivatives of the Acid A_1.

a-Ketohomocamphoric Acid,



Both the monomethyl derivative of the acid A_1 and the dimethyl derivative, or methoxy-ester, are decomposed by boiling 50 per cent. potassium hydroxide. In both instances, ammonia, without any detectable trace of methylamine, is evolved.

The decomposition is best carried out with the monomethyl derivative; here, in the initial stage of the reaction, the crystals change to an opaque mass, probably due to deposition of potassium salt, and this is soon converted into an oil. The oil quickly dissolves, and a sudden evolution of ammonia takes place. Action ceases after about ten minutes' boiling, when the solution may be cooled, acidified with hydrochloric acid, and extracted with ether, which removes a viscid, strongly acid oil. It was found exceedingly difficult to purify this product; at the end of some weeks' exposure it sets to a pulp, which may be triturated with concentrated hydrochloric acid, allowed to remain with it for some hours, and then transferred to porous earthenware. The white solid which is finally obtained in this manner can be further purified by dissolving it in the minimum quantity of anhydrous formic acid, and then adding concentrated hydrochloric acid until a permanent milkiness results. After some hours, a quantity of the substance is deposited in white needles, which can be separated and exposed over paraffin wax and potassium hydroxide in a vacuum for several days (Found: C=56·2, 58·4; H=6·9, 7·0. $C_{11}H_{16}O_5$ requires C=57·9; H=7·0 per cent.).

Samples titrated with alkali in the presence of phenolphthalein gave numbers for the equivalent somewhat wide of the mark, but showed the acid to be dibasic.

In spite of the unsatisfactory analytical data, there can be no doubt that the formula given represents the composition of the pure substance. The latter is excessively hygroscopic, but is nevertheless not readily soluble in water. It dissolves sparingly in benzene and still less readily in petroleum, but is freely soluble in alcohol, ether, acetone, or ethyl acetate; it does not appear to crystallise from any of these solvents, but separates as an oil. The acid in aqueous solution gives with ferric chloride a blue coloration, which disappears slowly in the cold and rapidly near 100°.

The *lead* salt is but slightly soluble in water. The *silver* salt is

sparingly soluble in cold water, but dissolves somewhat freely in hot; it is not rapidly decomposed on exposure to light.

When α-ketohomocamphoric acid is heated, it melts at 135—139° with slight decomposition; at 170°, the decomposition occurs rapidly, carbon monoxide and water being evolved, and a white, crystalline sublimate formed. This sublimate was purified by distillation in a current of steam and recrystallised from petroleum (Found: C = 66·2; H = 7·7. $C_{10}H_{14}O_3$ requires C = 66·0; H = 7·7 per cent.).

The product melted at 218—219°, and its identity with camphoric anhydride was completely established by the usual methods.

α-Ketohomocamphoric acid reduces boiling dilute copper sulphate solution; lead or manganese dioxides added to its warm aqueous solution instantly cause evolution of carbon dioxide with effervescence.

The *phenylhydrazone*, $CO_2H\cdot C_8H_{14}\cdot C(CO_2H){:}N_2HPh,H_2O$, was prepared by mixing the acid in about 1 per cent. aqueous solution with phenylhydrazine acetate; the solid which separated was crystallised from dilnte methyl alcohol (Found: C = 61·2; H = 7·6; N = 8·4. $C_{17}H_{22}O_4N_2,H_2O$ requires C = 60·8; H = 7·1; N = 8·3 per cent.).

The compound crystallises in needles and melts at 184°, with slight decomposition; it dissolves in aqueous sodium hydrogen carbonate, displacing carbon dioxide.

α-iso*Nitrosohomocamphoric Acid*, $CO_2H\cdot C_8H_{14}\cdot C({:}NOH)\cdot CO_2H$.

The ketonic acid (1 gram) was heated for an hour on the water-bath with a solution of free hydroxylamine (about 1 gram) in absolute alcohol. The oil obtained by subsequently removing the alcohol did not crystallise, and had to be purified by dissolving it in ether and shaking the solution repeatedly with water, drying, and evaporating to dryness. The clear oil dissolved completely in concentrated hydrochloric acid, and was precipitated on dilution with water.

The *iso*nitroso-acid itself did not reduce Fehling's solution, but, after boiling with dilute hydrochloric acid, gave all the tests for hydroxylamine. On treatment with bromine water, pyridine, and hydrogen peroxide (Piloty's test, *Ber.*, 1902, **35**, 3099), it was converted into a blue compound, which could be extracted by ether.

When heated in a vacuum, the *iso*nitroso-acid decomposed, giving a white sublimate; the latter is strongly acid, and when extracted with boiling water yields, somewhat tardily, crystals, which melt sharply at 148°; this product was compared with a sample of the α-nitrile of camphoric acid prepared from *iso*nitrosocamphor and acetic anhydride, and found to be identical with it.

It is noteworthy that α-ketohomocamphoric acid, its oxime, and also α-camphonitrile, are all difficult to obtain in stable, crystalline forms. This is possibly connected with the presence of the group $\cdot\dot{C}H$ in direct attachment to >CO, >C:NOH, and ·CN respectively, combinations which are associated with the ready occurrence of isodynamic (tautomeric) change.

Action of Ferrous Hydroxide and Alkali on the Acid A_1.

α-Camphidonecarboxylic Acid,
$$\begin{array}{l} CH_2.CH\text{---}CH\cdot CO_2H \\ \quad\;\; | \qquad\; CMe_2 \quad NH \\ CH_2\cdot CMe\text{---}CO \end{array}$$

Whilst most of the common reducing agents attack the acid A_1 either not at all or only with difficulty, the substance is very readily reduced by the following process.

The acid (5 grams) is dissolved in 20 per cent. potassium hydroxide (150 c.c.), the solution then added to one of crystallised ferrous sulphate (20 grams) in water (100 c.c.), and the whole heated at the boiling point for three hours. Some ammonia is evolved, and the dark precipitate finally becomes pale brown. After filtration, the clear, aqueous solution is acidified with hydrochloric acid and repeatedly extracted with ether, which, after drying and evaporating, furnishes about 4·2 grams of a white solid. The quantity of ammonia liberated in the foregoing operation was found to correspond with about 10 per cent. of the nitrogen present in the substance used; the nitrogen-free product has not been isolated.

The white solid, obtained as above, is best crystallised from acetone; from the cold solvent it separates in slender needles, which, if at once removed and dried, may be kept unaltered for some considerable time. If they are left in contact with the mother liquor, however, they soon become converted into plates, which represent the stable form of the compound.

The needle form, if heated, appears to undergo crystalline change at 190—200°, and subsequently liquefies at 230°; if heated suddenly to a high temperature, the needles do not melt instantaneously below about 234°, so that it is probable that their true melting point is somewhat higher even than this. The mass obtained by allowing the fused substance to solidify usually melts at about 205°, but it is uncertain what significance should be attached to this observation (Found: C = 62·2; H = 8·0; N = 6·6. $C_{11}H_{17}O_3N$ requires C = 62·6; H = 8·1; N = 6·6 per cent.).

The equivalent, determined by titration with sodium hydroxide,

using phenolphthalein, was 210; a monobasic acid, $C_{11}H_{17}O_3N$, requires 211.

The molecular weight was determined in phenol by the cryoscopic method, the number obtained being 205 (mean of three determinations) instead of 211, as calculated.

a-Camphidonecarboxylic acid is insoluble in light petroleum, moderately soluble in ether or water, and freely so in alcohol, ethyl acetate, acetic acid, or chloroform. Its solubility in water is greatly raised by the addition of hydrochloric acid.

The aqueous solution is strongly acid and gives no coloration with ferric chloride. An aqueous solution of the sodium salt gives no precipitate with salts of silver, lead, mercury, copper, calcium, barium, or iron; it rapidly discharges the colour of permanganate and bromine water.

The free acid is exceedingly stable. It is not affected by boiling 50 per cent. sulphuric acid or potassium hydroxide, or by heating in a sealed tube with concentrated hydrochloric acid at 180°. In small quantities, it can be distilled with only slight decomposition. It is not readily oxidised by chromic acid mixtures, and does not appear to react with acid chlorides, with nitrous acid, or with methyl sulphate.

It was ultimately found possihle to eliminate the carboxyl group by heating the *silver* salt. The latter was prepared by neutralising the acid in aqueous solution with silver carbonate, and formed long, colourless needles, which darkened on exposure to light; when cautiously heated in an atmosphere of carbon dioxide under diminished pressure, it decomposed and yielded a yellow sublimate. The latter was basic, and gave a characteristic picrate (m. p. 189—191°), which was purified by crystallisation, decomposed, and the free base recrystallised from light petroleum. The base formed arborescent leaflets melting at 230° (Found: C=71·7; H=10·2; N=8·2. $C_{10}H_{17}O_4N$ requires C=71·9; H=10·1; N=8·4 per cent.).

The characters of the base were almost precisely those ascribed to a-camphidone by Tafel and Eckstein (*Ber.*, 1901, **34**, 3280). Samples of the substance and its picrate were prepared from camphorimide, and direct comparison left no doubt as to the complete identity with the products above described.

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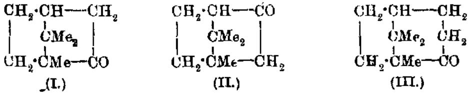
LXXIX.—*Homocamphor.*

By Arthur Lapworth and Frank Albert Royle.

Camphor (I) and the large group of compounds closely related to it have attracted an unusual amount of interest, owing to the difficulty with which they yielded up the secrets of their exact structures. The varied changes to which the molecules of these substances are prone are not less remarkable because the gross results of such transformations can now be represented graphically; and although analogies may be drawn between their transformations and those in some other series, little is yet known of their mechanism. Again, although several ketones nearly allied to camphor have been prepared, these have not, for the most part, been very closely investigated, and therefore peculiarities in the behaviour of camphor have not yet been clearly associated with irregularities in structure; it is not clear, for instance, what is the precise influence exerted by the methyl groups, or what would be the effect of a change in the size of the carbon rings. Epicamphor (II) is unique as an instance of a compound which is very closely related to camphor, and has been experimentally compared with camphor in nearly all interesting particulars (Bredt and Perkin, T., 1913, **103**, 2182).

In 1913, the authors had in view the desirability of studying a substance differing from camphor in one particular only, namely, in the inclusion of an additional $\cdot CH_2\cdot$ group in the ketone ring. This substance they have prepared, and propose to term *homocamphor* (III). It was originally hoped to make the research a

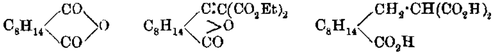


(I.) (II.) (III.)

fairly exhaustive one, but it was found that the preparation of homocamphor in sufficient quantity would be a very lengthy and costly undertaking, and the conditions which have succeeded the outbreak of war, when the work was interrupted, have made the project impracticable for the present. It has therefore been decided to describe the results which have already been obtained.

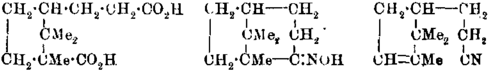
The first step in the synthesis of homocamphor consisted in the preparation of camphorylmalonic ester (V) from camphoric

anhydride (IV) and diethyl sodiomalonate by Winzer's method (*Annalen*, 1890, **257**, 298).



(IV.) (V.) (VI.)

By reduction of (V) (best carried out electrolytically under the conditions referred to in the experimental part) and subsequent hydrolysis, *hydrocamphorylmalonic acid* (VI) is obtained, and this is readily converted, on distillation, into carbon dioxide and Winzer's hydrocamphorylacetic acid (VII). The latter can be converted into homocamphor either by heating its lead salt in a current of carbon dioxide or by prolonged action of acetic anhydride, followed by distillation in a vacuum. Homocamphor

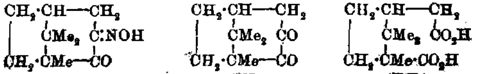


(VII.) (VIII.) (IX.)

forms a colourless, indefinitely crystalline mass closely resembling camphor in odour, taste, and in general behaviour towards solvents. Its optical rotatory power is, however, in the opposite sense to that of the camphor from which, through camphoric anhydride and the above series of reactions, it is prepared; it has $[\alpha]_D -112 \cdot 9°$ in benzene, whilst camphor has $[\alpha]_D +39 \cdot 1°$.

Homocamphor readily yields a *semicarbazone* and an *oxime* (VIII). The latter closely resembles camphoroxime, and has much the same peculiar odour as that substance; like camphoroxime, it develops a perfume resembling that of raspberries when heated with sulphuric acid, and this is doubtless due to the formation of homocampholenonitrile (IX). This product does not appear to be formed so readily as is campholenonitrile from camphoroxime, which fact seems to indicate a greater stability of the six-carbon ring as compared with the five-carbon ring in camphoroxime.

An *isonitroso*-derivative (X) may be obtained from homocamphor under conditions similar to those used in converting camphor into its *iso*nitroso-derivative, and closely resembles the latter in properties. By the action of acid formaldehyde on *iso*nitrosohomocamphor



(X.) (XI.) (XII.)

(compare Lapworth, T., 1896, **69**, 323), a small quantity of a volatile, yellow compound is obtained, and this much resembles camphorquinone, although it appears to be less intensely coloured; it is doubtless *homocamphorquinone* (XI).

In order to establish the structure of homocamphor, which in the absence of further data would have rested on the assumptions that Winzer's hydrocamphorylacetic acid has the structure (VII), and that no change of structure had attended the ring-closure at the succeeding step in the synthesis, advantage was taken of the ease with which cyclic *iso*nitroso-ketones, like *iso*nitrosocamphor, undergo the Beckmann change, becoming converted into amides or imides of the open-chain dicarboxylic acids. *iso*Nitrosohomocamphor was warmed with acetyl chloride, and the product hydrolysed with alkali; as was anticipated, *homocamphoric acid* (XII) was precipitated on addition of acid, so that there can be no question that the structures assumed for homocamphor (III) and its *iso*nitroso-derivative (X) are correct.

Experimental.

Camphorylmalonic ester was prepared by the condensation of ethyl sodiomalonate with camphoric anhydride in benzene, in accordance with Winzer's method (*loc. cit.*). It was obtained as a viscid, colourless liquid distilling at 218°/20 mm., and ultimately setting to a solid, which melted at 81° after recrystallisation from benzene. The yield fluctuated between 70 and 75 per cent. Attempts to shorten the time required for the condensation process by substituting toluene for benzene as solvent were not successful, and a trial of substituting camphoryl chloride for camphoric anhydride (Winzer, *loc. cit.*) did not give encouraging results.

For the *reduction* of camphorylmalonic ester, comparative tests of several methods were made. Winzer used sodium amalgam, allowing this to act on an alcoholic solution of the unsaturated ester, with such intermittent additions of sulphuric acid as were required to maintain a slightly acid reaction in the solution. He does not give the yield. In using this method, the present authors found that a decided improvement was effected by omitting the additions of sulphuric acid and employing instead a constant stream of carbon dioxide.

Much trouble was at first experienced in obtaining the hydrocamphorylmalonic acid in crystalline form, and the cause of this was ultimately traced to the fact that during the reduction the hydrolysis of the ester is not by any means so complete as Winzer's description would lead one to infer, and appreciable quantities of

the mono- and di-ethyl esters of hydrocamphorylmalonic acid are invariably left. It is therefore necessary, after the reduction itself is complete, to add to the solution a considerable excess of alkali and to heat for some time; when a portion of the liquid on acidification yields an acid which solidifies at once, the whole may be worked up in the usual manner. With these precautions, the authors were able to obtain yields of pure hydrocamphorylmalonic acid corresponding with 66 per cent. of that theoretically possible.

Many experiments were also made with the view of effecting the reduction electrolytically. A pure lead sheet, 20 × 30 cm., carefully polished, cleaned, and then covered with a deposit of spongy metal, was employed as cathode, and a sheet of platinum foil 5 × 2·5 cm. as anode. A clean, porous porcelain cell was used to contain the anode liquid (dilute sulphuric acid), and this was immersed in a beaker containing the cathode liquid. Glass spirals, through which cold water circulated, were immersed in the electrode chambers, and served for cooling purposes. The cathode liquid contained the unsaturated ester (20 grams) dissolved in a mixture of spirit (1500 grams) and concentrated sulphuric acid (150 grams). A current of 2 amperes at 10 volts was employed until reduction was complete, when the cathode liquor was completely hydrolysed with excess of alkali and worked up for hydrocamphorylmalonic acid. By this process, yields of 85 per cent. of the theoretical were normally obtained, but, like other similar reduction processes, success is uncertain unless the utmost care is exercised to ensure the purity of the fluids, electrodes, and cells.

Aluminium amalgam, used as reducing agent in diluted alcohol, gave yields of hydrocamphorylmalonic acid amounting to only 57 per cent. of the theoretical. Other methods of reduction, including the use of gaseous hydrogen and colloidal palladium, proved even less satisfactory.

The crude hydrocamphorylmalonic acid obtained by any of the above processes was converted into hydrocamphorylacetic acid by heating for an hour in an oil-bath at 180°, and then distilling in a vacuum; the fraction boiling at 260—270°/20 mm. yielded, as a rule, the pure hydrocamphorylacetic acid, melting at 142°, on recrystallisation from water. Occasionally, however, the product contained an impurity of an unsaturated character, in which case it was dissolved in sodium carbonate and left in contact with excess of permanganate for an hour, when it was subsequently recovered in satisfactory condition.

Dimethyl Hydrocamphorylacetate.

As one of the carboxyl groups of hydrocamphorylacetic acid is attached to a quaternary carbon atom, and is therefore resistent to the ordinary esterification processes, the dimethyl ester of the acid was prepared through the normal silver salt. The latter was readily obtained as an insoluble precipitate on addition of silver nitrate to the aqueous solution of the neutral sodium salt. The washed salt, dried at 110°, was boiled for three hours with methyl iodide dissolved in dry ether. The resulting ester was worked up in the usual manner, the main fraction being obtained as a colourless, viscid oil boiling at 175°/20 mm. Found: C=65·5; H=9·6. $C_{14}H_{24}O_4$ requires C=65·6; H=9·4 per cent.).

By cooling in liquid air and allowing the temperature slowly to rise, the oil set to a crystalline mass melting at about 25°.

An acid by-product, doubtless the *monomethyl* ester, was isolated during the working up of the diethyl ester; it distilled at 202—212°/19 mm. as a viscid, colourless oil which, wheu the interior of the containing tube was scratched with a glass rod, solidified to a mass of small needles.

When the above dimethyl ester is heated with excess of sodium methoxide at about 100°, the whole becomes brownish-red. On subsequently acidifying the solution, there is obtained a product which with ferric chloride gives a red coloration, soluble in amyl alcohol, and a copper derivative which is insoluble in water but soluble in alcohol. These facts point to the presence in this product of methyl homocamphorcarboxylate,

$$C_8H_{14}{<}{\substack{CH_2\\CO-}}{>}CH{\cdot}CO_2Me,$$

but this substance, from which it was hoped to prepare homocamphor, has not been closely examined, as the desired end was ultimately attained by a shorter route.

Homocamphor (III, p. 743).

This substance was obtained from hydrocamphorylacetic acid by the following processes:

(1) The acid was converted into its neutral sodium salt, and this, by double decomposition in aqueous solution with lead acetate, into the lead salt, which forms a heavy, white precipitate, and may be collected, washed with water and alcohol successively, and dried at 100°.

Ten grams of this salt were placed in a wide, hard-glass tube, which was slowly heated in an inclined position while a current of carbon dioxide was led through it from the higher end. The lower end of the tube was connected by means of an adapter to a flask, which served as a receiver, the issuing gases from the latter being passed through ether in order to retain the last traces of homocamphor. The crude product, after carefully evaporating off the ether used to collect it all, was a pale brown solid, and was purified by distillation in a current of steam.

(2) Homocamphorylacetic acid (8 grams) was boiled with acetic anhydride (20 grams) for several hours, and then allowed to remain at the ordinary temperature for some days. The acetic anhydride was subsequently removed by distillation, and the residue slowly heated *under diminished* pressure (12—20 mm.), the semi-solid distillate being warmed with aqueous sodium carbonate and distilled in a current of steam.

Homocamphor forms a white, indistinctly crystalline mass. In appearance, odour, and behaviour towards the usual media, it very closely resembles ordinary camphor, and, like that compound, is appreciably soluble in water, to which it communicates a camphoraceous odour. It was analysed after exposure in a vacuum desiccator over sulphuric acid (Found: C=79·3; H=10·9. $C_{11}H_{18}O$ requires C=79·5; H=10·9 per cent.).

Homocamphor melts at 189—190°, and sublimes readily far below this temperature. It is lævorotatory, and has $[\alpha]_D$ −112·9° in 4 per cent. solution in benzene.

Homocamphorsemicarbazone, $C_{11}H_{18}:N\cdot NH\cdot CO\cdot NH_2$.

This is readily obtained by boiling homocamphor in alcoholic solution with semicarbazide hydrochloride and sodium acetate for three hours. It crystallises from alcohol in slender, colourless needles melting and decomposing at 250—252°. The substance is very sparingly soluble in water, but dissolves readily in methyl or ethyl alcohol. Cold concentrated hydrochloric acid dissolves it and, on adding water, the semicarbazone is precipitated unchanged but, if steam is passed through the solution, pure homocamphor passes over.

Homocamphoroxime (VIII, p. 744).

This is prepared by dissolving homocamphor (1 gram) in alcohol adding solid hydroxylamine hydrochloride (0·8 gram) and sodium acetate (2—5 grams), and boiling the whole for two hours on the

water-bath. On cooling and diluting with water, the oxime is slowly deposited in crystals, which are collected and recrystallised from dilute methyl alcohol (Found: C=73·3; H=10·7; N=7·9. $C_{11}H_{19}ON$ requires C=72·9; H=10·5; N=7·7 per cent.).

This oxime much resembles camphoroxime in general behaviour towards organic solvent media, and has much the same peculiar odour as that substance. It crystallises from dilute methyl alcohol in long needles melting at 167—168°. When a small quantity of the oxime is heated with a drop of concentrated sulphuric acid, an odour very similar to that of campholenonitrile becomes perceptible; the quantities of material available did not admit of the product being isolated.

iso*Nitrosohomocamphor* (X, p. 744).

Homocamphor (3 grams) is dissolved in anhydrous ether (100 c.c.), and finely powdered sodamide (2 grams) is then added. The whole is stirred mechanically for two hours, then cooled to 0°, and maintained at this temperature while freshly distilled amyl nitrite (4·5 c.c.) is gradually introduced. After remaining overnight, the product is poured into ice-water, the aqueous layer separated, extracted repeatedly with ether, and then acidified with acetic acid. The precipitated solid (2 grams) is collected, washed with water, dried, and crystallised from a mixture of benzene and light petroleum.

The substance dissolves in all the usual organic media, and crystallises from water in long, slender needles, and from benzene and petroleum in small, flat plates. It melts at 167—168°.

It dissolves in formaldehyde (40 per cent.), and if the solution is warmed on the water-bath for two hours and then heated with excess of hydrochloric acid under a reflux condenser, minute, pale yellow crystals, which have a sweet, camphoraceous odour, collect in the condenser tube; these crystals doubtless consist of *homocamphorquinone* (XI, p. 744). The rate of formation of this compound is not so rapid as that of ordinary camphorquinone from *iso*nitrosocamphor in similar circumstances (compare Lapworth, *loc. cit.*), and as the yield was very small, sufficient could not be obtained for accurate characterisation or analysis.

Conversion of iso*Nitrosohomocamphor into Homocamphoric Acid.*

*iso*Nitrosohomocamphor (0·5 gram) was boiled with acetyl chloride for five hours, the solution then evaporated to dryness, and the solid residue boiled with 40 per cent. aqueous potassium hydroxide

for ten hours, during which time ammonia was slowly evolved. After a preliminary extraction with ether to remove neutral material, the alkaline liquid was acidified with sulphuric acid. The resulting brown acid which was precipitated proved to be highly insoluble in most of the ordinary organic media, but dissolved freely in boiling nitrobenzene, and, on cooling, separated in microscopic needles melting at 233°; its equivalent, determined by titration against $N/10$-sodium hydroxide, using phenolphthalein as indicator, was 106. The characters described are precisely those of *homocamphoric acid* (XII, p. 744), the calculated equivalent of which is 107.

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ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, MANCHESTER. [*Received, May 20th,* 1920.]

LXXX.—*The Nitration of Aceto*-m-*toluidide.*

By JAMES WILFRED COOK and OSCAR LISLE BRADY.

FROM the nitration products of *m*-toluidine, only 6-nitro-*m*-toluidine has been isolated, although evidence has been obtained that at least two of the other possible isomerides are formed in small quantities. Nitration in the presence of excess of concentrated sulphuric acid does not lead to meta-substitution. From aceto-*m*-toluidide, the 4- and 6-nitro-*m*-toluidines have been isolated, and this result has been confirmed by the present authors.

The dinitration of aceto-*m*-toluidide should, theoretically, give rise to three isomerides, and the reaction has been studied with the view of obtaining moderate quantities of 2:6-dinitro-*m*-toluidine for the synthesis of 2:3:6-trinitrotoluene.

Aceto-*m*-toluidide is added in small quantities at a time to ten times its weight of nitric acid (D 1·5) with thorough agitation, the temperature being kept below 25°; on pouring into water, a mixture of the dinitroaceto-*m*-toluidides separates as a pasty mass. This cannot be recrystallised satisfactorily, so is converted into a mixtnre of the amines by heating on the water-bath for an hour with 50 per cent. sulphuric acid, filtering off any tarry matter through glass wool, and diluting the filtrate with

water. The precipitated amines are collected, washed and dried, when a product is obtained which sinters at 90° and melts completely at 150°.

Separation of the Dinitro-m-toluidines.—The mixture of dinitro-*m*-toluidines is fractionally recrystallised from alcohol. The first fraction which separates from the hot alcohol melts at 170°, on diluting somewhat with water a second fraction melting at 145° is obtained and on completely precipitating the filtrate a third fraction melting at 92—93°.

By further recrystallisation of these fractions and combining the products of higher melting point, a compound melting at 193—194° is obtained, which proved to be 4:6-dinitro-*m*-toluidine. Its identity was established by the mixed melting-point method with the compound obtained by the action of ammonia on 3:4:6-trinitrotoluene (Hepp, *Annalen*, 1882, **215**, 371). This compound was not oriented by Hepp, and is incorrectly given as a derivative of *p*-toluidine in Richter's "Lexicon." The correct formula is assigned to it by Will (*Ber.*, 1914, **47**, 708), who obtained from it 2:4-dinitrotoluene by removal of the amino-group. The compound has also been oriented by one of us in several ways.

The fractions of lower melting point could not be separated by recrystallisation from alcohol, acetic acid or benzene, but if they are acetylated with acetic anhydride and the dinitroaceto-*m*-toluidides recrystallised from alcohol, 2:6-dinitroaceto-*m*-toluidide (m. p. 166°; Körner and Contardi, *Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339) separates first and can readily be obtained pure.

The identity of this compound was confirmed by hydrolysis to the amine (m. p. 131° crude; Körner and Contardi, *loc. cit.*, give 133·8°), removal of the amino-group by the diazo-reaction and identification of the 2:6-dinitrotoluene obtained by the mixed melting-point method.

No 2:4-dinitro-*m*-toluidine has been isolated from the nitration product and from a consideration of the relative solubilities of the three dinitro-*m*-toluidines and of their acetyl derivatives, and of the course of the fractional crystallisation of the mixture, it seems probable that little, if any, of this compound is formed in the nitration of aceto-*m*-toluidide.

In one experiment, on recrystallising the acetyl compounds from the fractions of lower melting point, a compound melting at 228—230° was the main product and this proved to be slightly impure 2:4:6-trinitroaceto-*m*-toluidide. It was thought that 2:4-dinitro-*m*-acetotoluidide might be more readily nitrated than the other isomerides, and for this reason not appear as such in the product; experiment has shown that this compound is not

nitrated under the conditions of experiment, and that more vigorous treatment leads to decomposition.

Nitration of 6-*Nitroaceto*-m-*toluidide.*—6-Nitroaceto-*m*-toluidide was at first prepared by Cohen and Dakin's method (T., 1903, **83**, 33), but later a modification was introduced which simplified the separation of the two isomerides formed.

To a mixture of 100 c.c. of nitric acid (D 1·5) and 25 c.c. of glacial acetic acid, cooled in ice, 20 grams of aceto-*m*-toluidide are added. After an hour, the mixture is poured into $1\frac{1}{2}$ litres of water and the solid which separates is collected at once. This melts at 101—102° and is almost pure 6-nitroaceto-*m*-toluidide, one crystallisation from alcohol yielding the pure substance. The filtrate, on remaining overnight, deposits more crystals which melt at 68—75°, one recrystallisation from alcohol giving pure 4-nitroaceto-*m*-toluidide.

The 6-nitroaceto-*m*-toluidide is added to excess of nitric acid (D 1·5), the temperature being kept below 25°, the mixture allowed to remain for an hour and poured into water. The pasty solid is extracted with ether, the ethereal solution washed with water, the solvent removed and the residue hydrolysed with 50 per cent. sulphuric acid. The amines, after precipitation by dilution, are separated in a manner similar to that described above. In this way 4:6- and 2:6-dinitroaceto-*m*-toluidides are obtained.

2:4- *and* 4:6-*Dinitro*- and 2:4:6-*Trinitro-aceto*-m-*toluidides.*

These compounds have been prepared for the purpose of identifying the various acetyl compounds obtained in the above reaction. They are obtained by warming the corresponding amines with acetic anhydride in the presence of one drop of concentrated sulphuric acid, pouring the product into water and recrystallising the precipitated acetyl derivative from alcohol.

2:4-*Dinitroaceto*-m-*toluidide* crystallises in colourless needles melting at 211—212°:

0·2895 gave 45·3 c.c. N_2 at 20·5° and 745 mm. N = 17·9.

$C_9H_9O_5N_3$ requires N = 17·6 per cent.

4:6-*Dinitroaceto*-m-*toluidide* crystallises in pale yellow needles melting at 103°:

0·2167 gave 33·8 c.c. N_2 at 18° and 746 mm. N = 18·0.

$C_9H_9O_5N_3$ requires N = 17·6 per cent.

2:4:6-*Trinitroaceto*-m-*toluidide* crystallises in microscopic, white, silky needles melting and decomposing at 249°:

0·1029 gave 17·8 c.c. N_2 at 18° and 751 mm. N = 19·9.

CHON requires N = 19·7 per cent.

Summarising, the main product of the dinitration of aceto-*m*-toluidide and of the nitration of 6-nitroaceto-*m*-toluidide is 4:6-dinitroaceto-*m*-toluidide. A smaller quantity of the 2:6-dinitro-compound is formed and little, if any, of the 2:4-dinitro-derivative.

ORGANIC CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, April 21st*, 1920.]

LXXXI.—*Studies in the Camphane Series. Part XXXVIII. The Cyanohydrazone of Camphorquinone.*

By MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE.

ALTHOUGH the aliphatic diazo-compounds have received increasing attention during recent years, their behaviour towards potassium cyanide has not been systematically studied. Peratoner and Palazzo (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 432, 501) noted the production of acetonitrile and methylcarbylamine from diazomethane and hydrogen cyanide, whilst Wolff (*Annalen*, 1902, **325**, 149) found that diazoacetophenone and potassium cyanide gave a product which he represented by the formula

$$C_6H_5 \cdot C(OK)\colon CH \cdot N\colon N \cdot CN,$$

and regarded as derived from acetophenoneazocyanide,

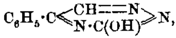
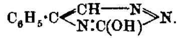
$$C_6H_5 \cdot CO \cdot CH_2 \cdot N\colon N \cdot CN;$$

he also described it as yielding "acetophenoneazocarbamide," $C_6H_5 \cdot CO \cdot CH_2 \cdot N\colon N \cdot CO \cdot NH_2$, with boiling dilute sulphuric acid. In a subsequent paper with Lindenhayn (*Ber.*, 1903, **36**, 4126), the possibility of acetophenoneazocyanide being phenylglyoxalcyanohydrazone, $C_6H_5 \cdot CO \cdot CH\colon N \cdot NH \cdot CN$, was indicated, but evidently not preferred, by Wolff, because in a much later paper with Greulich (*Annalen*, 1912, **393**, 41) the corresponding product from diazoacetone was represented by the formula

$$CH_3 \cdot CO \cdot CH_2 \cdot N\colon N \cdot CN.$$

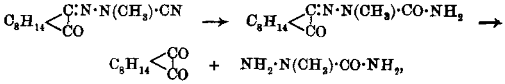
Diazocamphor being now a convenient material in which to observe the behaviour of the diazo-group, we have prepared from it by the action of potassium cyanide a compound which can scarcely be other than the cyanohydrazone of camphorquinone, because it dissolves in sodium carbonate and is hydrolysed very readily by acids to the α-semicarbazone. It seems to follow that the alternative grouping, $CH \cdot N\colon N \cdot CN$, adopted by Wolff is

excluded, and that his "acetophenoneazocarbamide" is really phenylglyoxalsemicarbazone, the phenylhydroxytriazine derived *from it being, therefore,*

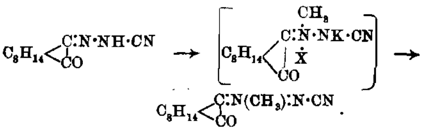
 instead of 

It is thus 5-phenyl-3-oxy-1:2:4-triazine, strictly comparable with 5:6-diphenyl-3-oxy-1:2:4-triazine prepared by Thiele and Stange (*Annalen*, 1894, **283**, 27) from benzilsemicarbazone, and with camphaneoxytriazine from camphorquinone-β-semicarbazone (Forster and Zimmerli, T., 1910, **97**, 2176).

Unfortunately, the readiness with which the cyano-group in the cyanohydrazone undergoes hydrolysis has precluded the isolation of cyanohydrazine, $NH_2 \cdot NH \cdot CN$, which was one of the objects of our inquiry. Moreover, finding that a methyl derivative is readily obtained from the cyanohydrazone, and thus hoping to arrive at methylcyanohydrazine, $NH_2 \cdot N(CH_3) \cdot CN$, we encountered another unforeseen obstacle. Not only did the cyano-group undergo hydrolysis with equal readiness, but the methylsemicarbazide obtained by complete hydrolysis of the camphorquinonemethylcyanohydrazone is uot 2-methylsemicarbazide, as would be expected from the changes,



but an *isomeric substance melting at 91·5° instead of 113°.* In view of the indifference towards benzaldehyde shown by this isomeride, the only conclusion to be drawn is that it is the missing 1-methylsemicarbazide, $CH_3 \cdot NH \cdot NH \cdot CO \cdot NH_2$, and that methylation of the cyanohydrazone has proceeded as follows:



Support is given to this conjecture by the fact that whilst the cyanohydrazone is colourless and has $[M]_D$ 574°, the methyl derivative is bright yellow and has $[M]_D$ 1460°; since the α-semicarbazone with $[M]_D$ 619° and the methylsemicarbazone are also colourless, it is reasonable to conclude that the cyanohydrazone, which

passes into the semicarbazone so readily, is closely allied to it in structure, and that this has become modified in methylation. Some analogy to such a change is offered by the alkylation of oximes, the products of which may be referred to both types, C:NOH and C:NH:O.

When hydrolysis of camphorquinonecyanohydrazone is effected with mineral acids in methyl or ethyl alcohol, the *a*-semicarbazone is accompanied by a basic material, the composition of which is that of the cyanohydrazone increased by the elements of the alcohol employed. These compounds are indifferent towards alcoholic potassium hydroxide or benzoyl chloride, but are converted into camphorquinone and its semicarbazone by hydrochloric acid; this behaviour and origin suggest that the bases are

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C(O\cdot CH_3):NH\\ |\\ CO\end{matrix} \quad \text{and} \quad C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C(O\cdot C_2H_5):NH\\ |\\ CO\end{matrix}$$

representing a new class of compounds, namely, imino-ethers of a semicarbazone.

EXPERIMENTAL.

Camphorquinonecyanohydrazone, $C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot CN\\ |\\ CO\end{matrix}$.

Whilst diazocamphor is completely transformed into the potassium derivative of the cyanohydrazone when an alcoholic solution remains for several days in contact with finely powdered potassium cyanide, action is more expeditious when the salt is dissolved in the minimum quantity of water. A solution containing 20 grams of diazocamphor in 100 c.c. of alcohol was therefore mixed with 25 grams of potassium cyanide in 50 c.c. of water, alcohol being then added in quantity just sufficient to form a clear liquid. After four days, the solution was diluted largely with water and extracted three times with ether, the faintly yellow, aqueous portion being then deprived of the major part of its ether-content by cold exhaustion during one hour at the water-pump. Acidification with dilute hydrochloric acid precipitated the cyanohydrazone in glistening, almost colourless crystals, the filtrate, which still contained ether, depositing a small additional quantity on keeping; the product weighed 19 grams. If the partial removal of ether prior to precipitation is omitted, addition of acid separates an ethereal layer, which maintains the cyanohydrazone in solution, besides impairing the quality of the product. The substance was purified by dissolution in 2½ parts of acetone, to which 6 parts of petroleum (b. p. 65°) were then added, pearly leaflets being precipitated; it becomes red at 141°, evolves gas at 204°, and a few

degrees above this temperature melts indefinitely to a red liquid (Found: C=64·53; H=7·27; N=20·52. $C_{11}H_{15}ON_3$ requires C=64·39; H=7·31; N=20·49 per cent.). The cyanohydrazone dissolves in alkali carbonates, and is readily soluble in organic media, excepting petroleum. A solution containing 0·3005 gram in 25 c.c. of 10 per cent. sodium carbonate gave α_D 4°21′ in a 1-*dcm. tube, whence* $[\alpha]_D$ *361·9°, which did not change* during five weeks when protected from light; on exposure, however, the liquid rapidly became yellow and turbid. When examined immediately a solution containing 0·3000 gram in chloroform diluted to 25 c.c. gave α_D 3°21′ in a 1-dcm. tube, rising during nine days to 3°37′ and subsequently falling; thus, the rotatory power in this solvent varies between $[\alpha]_D$ 279·1° and 301·4°. In alkaline solution, the cyanohydrazone is reduced by zinc dust or sodium "hydrosulphite" to aminocamphor (identified as the benzoyl derivative), but it does not couple with benzenediazonium chloride.

The yellow *compound* into which the cyanohydrazone changes when the *solid, or its solution in sodium carbonate, is exposed to* light, appears to be the isomeride arising from the transformation

$$C_8H_{14}<\begin{matrix}C{:}N{\cdot}NH{\cdot}CN\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH{\cdot}N{:}N{\cdot}CN\\ |\\ CO\end{matrix} ;$$

it crystallises from alcohol in silky, yellow needles containing the solvent, and was therefore precipitated from benzene by petroleum (Found: C=64·18; H=7·43). The substance becomes red at 182°, evolving gas at 189°, and passing to a viscous, red liquid at 193°; it yields camphorquinone when heated with dilute sulphuric acid.

The *methyl* derivative of the cyanohydrazone was prepared by shaking 20 grams dissolved in 80 c.c. of 10 per cent. sodium carbonate with 12 grams of methyl sulphate, and separated after thirty minutes in sulphur-yellow needles, weighing 19 grams; it *melts at 135° after recrystallisation from methyl alcohol, separating* in lustrous, transparent, six-sided plates (Found: C=65·29; H=7·85; N=19·26. $C_{12}H_{17}ON_3$ requires C=65·75; H=7·76; N=19·18 per cent.). It crystallises from boiling water in long pale yellow needles, and is not volatile in steam. A solution containing 0·2000 gram in chloroform diluted to 25 c.c. gave α_D 5°20′ in a 1-dcm. tube, whence $[\alpha]_D$ 666·6°.

The *benzoyl* derivative, prepared by the Schotten-Baumann process, crystallises from alcohol in long, colourless, striated plates melting at 155° (Found: N=13·71. $C_{18}H_{19}O_2N_3$ requires N=13·59 per cent.). A solution containing 0·2016 gram in chloroform diluted to 25 c.c. gave α_D 2°25′ in a 1-dcm. tube

whence $[\alpha]_D$ 299·6°. Under conditions which led to hydrolysis of the cyanohydrazone, the benzoyl derivative remained unchanged.

The *acetyl* derivative was produced in the course of two days when the cyanohydrazone remained suspended in two parts of acetic anhydride, and, after crystallisation from glacial acetic acid, melts at 104° (Found: N=16·98. $C_{13}H_{17}O_2N_3$ requires N=17·00 per cent.). A solution containing 0·2048 gram in chloroform diluted to 25 c.c. gave α_D 2°50′ in a 1-dcm. tube, whence $[\alpha]_D$ 345·8°.

Attempts to prepare benzyl, *p*-toluenesulphonyl, and hydroxyethyl derivatives of the cyanohydrazone were unsuccessful.

Action of Acids on Camphorquinonecyanohydrazone.

The course of hydrolytic change undergone by the cyanohydrazone varies materially with experimental conditions. Thus cold concentrated sulphuric acid liberates gas, whilst 50 per cent. acid produces hydrazine and camphorquinone in a few minutes when warmed. With oxalic acid in hot alcohol, the α-semicarbazone of camphorquinone is formed, and this arises also when the cyanohydrazone, dissolved in alcohol, remains during several days with hydrochloric or sulphuric acid; simultaneously, there is formed a basic substance, melting at 79·5°, when ethyl alcohol is used, and a lower homologue, melting at 133°, along with azocamphanone when methyl alcohol is the solvent.

Twenty grams of the cyanohydrazone dissolved in 30 grams of alcohol were left with 32 grams of concentrated hydrochloric acid during ten days, in which period there separated lustrous, colourless plates, augmented to 5·8 grams by dilution with water; this was identified with the α-semicarbazone by complete analysis and a melting point of the mixture. The quantity obtained from 10 grams of the cyanohydrazone in 20 grams of alcohol with 15 grams of sulphuric acid was very small, but a 50 per cent. yield was produced by hydrochloric acid when methyl in place of ethyl alcohol was used.

The Accompanying Bases.—On rendering alkaline with sodium carbonate the filtrate from semicarbazone, there was precipitated a yellow, granular *base*, weighing 8 grams in the above experiment with hydrochloric acid and 7 grams in that with sulphuric acid, which is thus more favourable to its production. After being twice recrystallised from alcohol diluted with water, it melts at 79·5°, separating in long, lustrous, pale yellow needles (Found: C=62·06; H=8·46; N=16·73. $C_{13}H_{21}O_2N_3$ requires C=62·15; H=8·36; N=16·73 per cent.). A solution containing 0·2000 gram in chloroform diluted to 25 c.c. gave α_D 2°14′ in a 1-dcm. tube,

whence $[\alpha]_D$ 279·1°. The substance is indifferent towards alcoholic potassium hydroxide, but when warmed with hydrochloric acid yields a mixture of camphorquinone with the α-semicarbazone; a suspension in sodium hydroxide is unchanged by benzoyl chloride.

The homologue was prepared by carefully mixing the cyanohydrazone (10 grams) dissolved in methyl alcohol (20 grams) with concentrated sulphuric acid (15 grams). After one week, liberal dilution with water precipitated a small amount of azocamphanone, the filtrate giving a deep yellow, viscous product when rendered alkaline. This was washed and set aside for many weeks, during which time it gradually became friable, and was then extracted several times with hot petroleum (b. p. 65°), which removed a very small quantity of a yellow, crystalline material melting at 86°. A solution of the residue in cold methyl alcohol was diluted with water until turbid, and the clear liquid decanted next day from an oily deposit; a yellow, solid *base* then separated, and melts at 133° after recrystallisation from methyl alcohol (Found. C = 60·95; H = 8·27; N = 17·66. $C_{12}H_{19}O_2N_3$ requires C = 60·76; H = 8·01; N = 17·72 per cent.). A solution containing 0·2023 gram in chloroform diluted to 25 c.c. gave α_D 2°9′ in a 1-dcm. tube, whence $[\alpha]_D$ 265·7°.

Hydrolysis of the Methyl Derivative of Camphorquinonecyanohydrazone.

The conditions which produce the α-semicarbazone from the cyanohydrazone did not lead to the corresponding methyl derivative from the methylated cyanohydrazone; instead, the hydrazine residue appears to be removed in the form of 1-methylsemicarbazide, associated with a *compound* having the empirical formula of the original methyl derivative, but melting at 101°.

The methyl derivative (10 grams) in alcohol (30 grams) was left with anhydrous oxalic acid (4·1 grams) during ten days, when the solution had deposited colourless, silky needles (0·65 gram). These having been filtered, liberal dilution with water precipitated a yellow, viscous product (6·8 grams), from which steam removed camphorquinone (1·4 grams); by treatment with alcohol, the sticky residue yielded a pale yellow substance, which melts at 101° after crystallisation from petroleum (Found: C = 66·08; H = 8·05; N = 19·01. $C_{12}H_{17}ON_3$ requires C = 65·75; H = 7·76; N = 19·17 per cent.). This product yielded camphorquinone with hydrochloric acid, and its formation was not observed when the methyl derivative was heated with oxalic acid in alcohol under reflux instead of remaining at the ordinary temperature. Thus the former pro-

cedure is preferable for obtaining the 1-methylsemicarbazide *oxalate*, 1·2 grams of which was produced from 6·6 grams of the methylated cyanohydrazone. It is freely soluble in water, from which alcohol precipitates it in colourless, silky needles; it melts and effervesces at 171° (Found: N = 23·74. $C_2H_7ON_3,C_2H_2O_4$ requires N = 23·46 per cent.).

1-*Methylsemicarbazide* was isolated by heating the oxalate in water with calcium carbonate until effervescence ceased, evaporating the filtrate to dryness, and extracting the residue with boiling benzene, which deposited colourless, pearly leaflets melting at 91·5° (Found: N = 47·01. $C_2H_7ON_3$ requires N = 47·19 per cent.). It rapidly gives a mirror with ammoniacal silver oxide, and reduces Fehling's solution on boiling, but it does not combine with benzaldehyde. The oxalate was also obtained by decomposing the methyl derivative of the cyanohydrazone (10 grams) in alcohol (40 grams) with sulphuric acid (5 grams) at the ordinary temperature, diluting largely after ten days, filtering from camphorquinone (2·6 grams), neutralising with barium carbonate, and evaporating the filtrate until pasty; on dissolving in alcohol and adding oxalic acid, the oxalate (0·7 gram) slowly separated.

Attempts to prepare 1-methylsemicarbazide by indirect methods for comparison with the foregoing product were unsuccessful. Benzylidenesemicarbazone (which melts at 225°, instead of 214° as stated in the literature) could not be methylated by methyl sulphate in boiling benzene or in cold alkali, and the action of benzoyl chloride in pyridine led to *s*-benzoylbenzylidenehydrazine, $C_6H_5\cdot CH{:}N\cdot NH\cdot CO\cdot C_6H_5$, melting at 208° (Found: C = 75·18; H = 5·45; N = 12·50. Calc.: C = 75·00; H = 5·35; N = 12·50 per cent.). On the other hand, when acetonesemicarbazone is treated with benzoyl chloride in pyridine, the product is benzoylsemicarbazide, melting at 222°. In this connexion, it should be mentioned that the *oxalate* of 2-methylsemicarbazide, prepared for comparison with the foregoing salt, melts and effervesces at 155° (Found: N = 31·69. $(C_2H_7ON_3)_2,C_2H_2O_4$ requires N = 31·34 per cent.). It crystallises from hot water in transparent prisms, and is very sparingly soluble in alcohol.

Camphorquinonemethylsemicarbazone $C_8H_{14}<\begin{matrix}C{:}N\cdot N(CH_3)\cdot CO\cdot NH_2\\ CO\end{matrix}$.

Having regard to the abnormal behaviour of camphorquinonecyanohydrazone on methylation, brought to light by the production of 1-methylsemicarbazide on hydrolysing the product, it was thought desirable to methylate the *a*-semicarbazone. Action in this case is normal, the methylated semicarbazone being identical

with the substance obtainable from camphorquinone by condensation with 2-methylsemicarbazide.

The α-semicarbazone (4·7 grams), dissolved in 10 per cent. sodium hydroxide (10 c.c.) and sufficient water to form a clear solution, was shaken with methyl sulphate (4 grams), when a colourless solid (4·6 grams) was precipitated. Being very soluble in alcohol, liberal dilution with water was necessary before it crystallised in colourless, triangular plates; it melts and evolves gas at 176°, and rapidly becomes bright yellow on exposure to light. In view of the misleading results of analysis, which pointed at first to a dimethyl derivative, the same compound was prepared also from camphorquinone (6 grams) and 2-methylsemicarbazide (3·3 grams) in alcohol, when it was found to contain water of crystallisation (Found: C = 58·17, 58·27; H = 8·18, 8·27; N = 17·07. $C_{12}H_{19}O_2N_3,\frac{1}{2}H_2O$ requires C = 58·54; H = 8·13; N = 17·07 per cent.). A solution containing 0·2051 gram in chloroform diluted to 25 c.c. gave α_D 3°30′ in a 1-dcm. tube, whence $[\alpha]_D$ 426·6°. On hydrolysis with aqueous sulphuric acid and removal of camphorquinone by ether, the remaining liquid gave benzylidenemethylsemicarbazone (m. p. 162°) with benzaldehyde.

Further Changes undergone by Diazocamphor.

Concurrently with the foregoing, attempts have been made to bring diazocamphor into combination with various agents likely to attack the diazo-group. For instance, it seemed probable that the triketone, $C_8H_{14}<\begin{matrix}CCl\cdot CO\cdot CCl\\ CO \quad\quad OC\end{matrix}>C_8H_{14}$, or, alternatively, the chloride of chlorocamphorcarboxylic acid, $C_8H_{14}<\begin{matrix}CCl\cdot COCl\\ CO\end{matrix}$, might arise by the action of carbonyl chloride, since Staudinger has found that diphenyldiazomethane is thus converted into diphenylchloroacetyl chloride (*Ber.*, 1916, **49**, 1939); although nitrogen is disengaged slowly, however, the action leads only to Angeli's camphenone, the ketone produced on heating diazocamphor. The constitution of this has been recently shown by Bredt and Holz (*J. pr. Chem.*, 1917, [ii], **95**, 133) to be that of a *β-pericyclo*camphanone. Unsuccessful, also, were attempts to couple the diazo-group with, or to displace it by, nitromethane, ethyl malonate, picryl chloride, or phenylacetonitrile.

It has been already observed (*T.*, 1910, **97**, 2171) that ammonium sulphide reduces diazocamphor to a mixture of the α- and β-hydrazones of camphorquinone; other reducing agents, such as sodium "hydrosulphite," stannous chloride in ether, an aluminium–mercury

couple, and aluminium in sodium hydroxide, transform it into camphor. In view of a recent paper by Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 554), who obtained nitrones of the general formulæ R·CH:NX:O and R_2·C:NX:O by the action of aromatic nitroso-derivatives on aliphatic diazo-compounds, we heated diazocamphor with *nitrosobenzene*, obtaining *camphoryl-N-phenylnitrone* (*iso*nitrosocamphor-*N*-phenyl ether), corresponding with the *N*-methyl (T., 1904, **85**, 896) and the *N*-ethyl (T., 1908, **93**, 251) ethers already prepared from sodium *iso*nitrosocamphor and the alkyl iodides. Attempts to produce analogous derivatives from nitrosodimethylaniline, nitrosodiphenylamine, and nitrosocarbazole failed.

The N-*Phenyl Ether of* iso*Nitrosocamphor*,

$$C_8H_{14}<\begin{matrix}C:NPh:O\\|\\CO\end{matrix}.$$

Diazocamphor (4·5 grams) and nitrosobenzene (2·6 grams) were heated together at 65° until gas evolution became brisk, when the tube was withdrawn and cooled; the diminished action was alternately stimulated and checked until it was safe to heat the mixture continuously. The deep green colour gradually faded to pale brown, and when gas no longer emerged, the product was set aside until crystals appeared. These were augmented by adding petroleum, from which the substance was recrystallised in lustrous, yellow needles melting at 78° (Found: C=74·48; H=7·63; N=5·53. $C_{16}H_{19}O_2N$ requires C=74·71; H=7·39; N=5·44 per cent.). A solution containing 0·2037 gram in chloroform, diluted to 25 c.c., gave α_D 0°45′ in a 1-dcm. tube, whence $[\alpha]_D$ 92·0°. Reduction with aluminium–mercury in ether gave phenylaminocamphor.

In conclusion, we desire to express our thanks to the Managers of the Royal Institution for their courtesy in placing a laboratory at our disposal.

SALTERS' INSTITUTE OF INDUSTRIAL CHEMISTRY,
ST. SWITHIN'S LANE, E.C. 4. [*Received, May 12th, 1920.*]

LXXXII.—*Organo-derivatives of Bismuth. Part III The Preparation of Derivatives of Quinquevalent Bismuth.*

By Frederick Challenger and Archibald Edwin Goddard.

With the object of preparing salts of the unknown compounds Ph_3BiO or $Ph_3Bi(OH)_2$, the action of aqueous potassium hydroxide and moist silver oxide on triphenylbismuthine dichloride has been investigated under various conditions. In all cases, triphenylbismuthine is regenerated. The same result is obtained if the dibromide is treated with alcoholic sodium hydroxide. Triphenylstibine dibromide when similarly treated yields triphenylstibine dihydroxide (Michaelis and Reese, *Annalen*, 1886, **233**, 50). If the solution obtained from triphenylbismuthine dichloride and aqueous alkali is treated with acetic, tartaric, or a similar organic acid, mixtures are obtained which contain dichloride and basic chloride, and very little, if any, acetate or tartrate. Better results were obtained with the carbonate described, but not analysed, by Michaelis and Marquardt (*Annalen*, 1889, **251**, 330). This compound with acetic acid gives *triphenylbismuthine acetate* $Ph_3Bi(OAc)_2$. The corresponding camphorsulphonate and lactate appear to be formed, and are now under investigation. With hydriodic acid, the carbonate reacts at the ordinary temperature with the formation of a red compound, which is probably the one already described by Challenger and Allpress (T., 1915, **107**, 21). Similar results were obtained by triturating the carbonate with water and iodine. This is further evidence of the instability of triphenylbismuthine di-iodide, which cannot be prepared from triphenylbismuthine and iodine. Triphenylbismuthine dichloride dissolves in cold concentrated sulphuric acid, giving *triphenylbismuthine sulphate*, which does not melt at 284°. Very little bismuth sulphate is produced in this reaction if rise of temperature is avoided, but the amount increases if the solution in sulphuric acid is left for several hours before pouring into water. Solution in ammonia and treatment with hydrochloric acid converts the sulphate into the *basic chloride*, which, on warming with concentrated hydrochloric acid, gives the dichloride. The basic chloride $Ph_3Bi(OH)Cl$ (m. p. 160—161°), is formed in various reactions for example, (*a*) by the action of moist ammonia gas on triphenylbismuthine dichloride in chloroform solution (a method by which the *basic bromide*, m. p. 150—151°, has also been prepared)

(*b*) from sodium and the dichloride in ether containing a trace of moisture; (*c*) by the action of aqueous ammonia on the dichloride. Up to the present, however, this compound has not been obtained from the dichloride by means of water or aqueous alcohol, according to which method Stilp * (*Diss.*, Rostock, 1910) prepared the basic bromides of tri-*p*-tolyl- and trixylyl-bismuthines.

When warmed with concentrated hydrochloric acid, it gives the dichloride. The action of acetic acid on the basic chloride gives rise to the dichloride and a compound, which is probably the acetate, in which case the reaction may be represented thus:

$$2(C_6H_5)_3Bi(OH)Cl = (C_6H_5)_3BiCl_2 + (C_6H_5)_3Bi(OH)_2,$$
$$(C_6H_5)_3Bi(OH)_2 + 2CH_3\cdot CO_2H = (C_6H_5)_3Bi(O\cdot CO\cdot CH_3)_2 + 2H_2O.$$

This is analogous to the action of acetic acid on the basic bromide of diphenyltelluride, $Ph_2Te(OH)Br$, which gives rise to the dibromide, and probably the diacetate (Lederer, *Annalen*, 1912, **391**, 335).

With magnesium methyl iodide, the basic chloride does not give triphenylmethylbismuthonium hydroxide, $Ph_3Bi(OH)CH_3$, but the dichloride and triphenylbismuthine, which points to the instability of the hydroxide. Triphenylmethylarsonium hydroxide, however, is a crystalline compound melting at 125—126°, prepared by the action of moist silver oxide on the iodide (Michaelis, *Annalen*, 1902, **321**, 166).

The action of copper bronze on triphenylbismuthine dichloride leads to the production of diphenylchlorobismuthine, probably owing to the prolonged action of heat, and not to contact with the copper. No compound of the type $Ph_3Bi\vdots BiPh_3$ was isolated.

In this connexion, it is worthy of note that triphenyl- and tri-*p*-tolyl-bismuthines and arsines, and also tri-*a*-naphthylbismuthine and triphenylbismuthine dichloride, have the normal molecular weight in benzene solution. Complexes of the type $R_3M\vdots MR_3$, which might possibly arise owing to the unsaturated nature of these organo-metallic or metalloidal compounds, do not appear to be formed.

The abnormal behaviour of the halogen derivatives of the bismuthines towards the Grignard reagent has been referred to in previous papers.† It is further exemplified by the fact that triphenylbismuthine is the principal product obtained when

* The results described in this dissertation do not appear to have been published elsewhere.

† Better results may possibly be obtained by modifying the conditions of reaction with the Grignard reagent, or by the use of organo-zinc or mercury derivatives. Experiments in this direction are in progress.

magnesium *p*-tolyl bromide reacts with triphenylbismuthine dichloride and diphenylbromobismuthine, and in the reaction between triphenylbismuthine dichloride and magnesium α-naphthyl bromide. Lederer (*Ber.*, 1911, **44**, 2287) has shown that triphenyltelluronium chloride yields diphenyltelluride and diphenyl when treated with magnesium phenyl bromide, whilst di-*o*-anisyltelluride dibromide is reduced to di-*o*-anisyltelluride on treatment with magnesium methyl iodide [(*Ber.*, 1920, **53**, 713). Compare also the remarkable instability of the mixed mercury diaryls (Hilpert and Grüttner, *Ber.*, 1915, **48**, 406)].

Iodine trichloride reacts with triphenylbismuthine, producing the dichloride and iodobenzene.

Tri-α-naphthylbismuthine dichloride was prepared by the action of chlorine on the bismuthine; Stilp (*loc. cit.*) was unable to obtain this compound. Like triphenylbismuthine dichloride, it is more stable than the corresponding dibromide.

The action of moist silver oxide in acetone is similar to that observed with triphenylbismuthine dichloride, and gives rise to tri-α-naphthylbismuthine.

Diphenyl-α-naphthylbismuthine has been previously described (T., 1914, **105**, 2216). Since attempts to obtain other mixed bismuthines have failed, the reaction between diphenylbromobismuthine and magnesium α-naphthyl bromide has been further studied. Whilst the mixed bismuthine has again been obtained and diphenyl-α-naphthylbismuthine dibromide analysed, the main product of the reaction consists of triphenylbismuthine.

Michaelis and Marquardt (*Annalen*, 1889, **251**, 320) observed that excess of ammonium sulphide decomposed triphenylbismuthine dibromide according to the equations:

(1) $(C_6H_5)_3BiBr_2 + (NH_4)_2S = (C_6H_5)_3Bi + 2NH_4Br + S$; *
(2) $2(C_6H_5)_3Bi + 3H_2S = 6C_6H_6 + Bi_2S_3$.

We have found that this reaction can be made the basis for the estimation of bismuth in substances of an analogous composition which, unlike the tertiary bismuthines, do not yield bismuth chloride with hydrochloric acid.

Triphenylstibine dihaloids do not react thus with hydrogen sulphide in alcoholic ammonia, but yield triphenylstibine sulphide. The bismuthine is therefore less stable than the corresponding stibine.

* In the absence of excess of hydrogen sulphide the bismuthine only is obtained.

Experimental.

Action of Moist Silver Oxide on Triphenylbismuthine Dichloride.

(*a*) *In the Cold.*—Two grams of triphenylbismuthine dichloride, about 30 c.c. of acetone, 0·93 gram of silver oxide, and 1 c.c. of water were shaken on a machine for sixteen hours, when 1·1 grams of triphenylbismuthine (m. p. 78°) were obtained from the acetone solution. The residue consisted of silver oxide, silver chloride, and a trace of bismuthine.

(*b*) *At about* 60°.—Five grams of triphenylbismuthine dichloride and 2·3 grams of silver oxide were heated in moist acetone on a water-bath for one hour. After removing the silver chloride and unchanged silver oxide, 3·2 grams of triphenylbismuthine were obtained.

Action of Alcoholic Potassium Hydroxide on Triphenylbismuthine Dichloride.

(*a*) *In the Cold.*—Three grams of triphenylbismuthine dichloride and 0·7 gram of potassium hydroxide in absolute alcohol were shaken for five and a-half hours.

Two kinds of crystals separated on keeping, (*a*) stout needles, and (*b*) small, fine needles mixed with a heavy powder, which were extracted with absolute alcohol, leaving potassium chloride. The alcoholic extract yielded triphenylbismuthine (m. p. 78—80°). The crystals (*a*) were found to be triphenylbismuthine dichloride.

The main bulk of the mixture was evaporated, when more triphenylbismuthine was obtained.

(*b*) *At the Boiling Point.*—Five grams of triphenylbismuthine dichloride in absolute alcohol were boiled for three hours with 1·2 grams of potassium hydroxide, and the solution filtered. From the filtrate, three deposits, (*a*), (*b*), and (*c*), were obtained. The crystals (*a*) melted at 138°, contained halogen, and most probably consisted of a mixture of triphenylbismuthine, triphenylbismuthine dichloride, and the basic chloride (see p. 768).

Deposit (*b*) was shaken with cold light petroleum; the extract deposited triphenylbismuthine, the insoluble portion yielding unchanged dichloride (m. p. 120—121°).

Deposit (*c*) was heated with water, the soluble portion yielding triphenylbismuthine (m. p. 78°); the insoluble residue consisted chiefly of potassium chloride.

Action of Aqueous Potassium Hydroxide on Triphenylbismuthine Dichloride.

Three grams of triphenylbismuthine dichloride, 0·7 gram of potassium hydroxide, and 30 c.c. of water were shaken in the cold for five and a-half hours, and the mixture was filtered. The residue was triphenylbismuthine dichloride. The filtrate was evaporated to dryness and treated with absolute alcohol, which removed potassium chloride. The solution was evaporated, and the residue, after crystallisation from light petroleum, melted at 77—78°, and did not depress the melting point of triphenylbismuthine.

Attempts to Isolate Triphenylbismuthine Dihydroxide or Triphenylbismuthine Oxide.

(1) Triphenylbismuthine dichloride was treated with aqueous potassium hydroxide in the cold as before, and the solution extracted three times with ether. The extract became cloudy on keeping, possibly owing to the absorption of atmospheric carbon dioxide. A solid finally separated which, on crystallisation from petroleum, melted at 74°. This was shown to be impure triphenylbismuthine. The aqueous portion also became cloudy and deposited triphenylbismuthine, which melted at 78—79° after crystallisation from alcohol. No compound corresponding with a dihydroxide or oxide was isolated.

(2) Triphenylbismuthine dibromide was dissolved in alcoholic sodium hydroxide, and the precipitate of sodium bromide filtered off. No further deposit was noticed after the solution had remained for a week. Part of the alcohol was therefore evaporated, when long needles of triphenylbismuthine were deposited.

Preparation of Michaelis's so-called Basic Carbonate.

Triphenylbismuthine dibromide (m. p. 122—124°) was suspended in alcohol and treated with excess of solid sodium hydroxide. Carbon dioxide was passed through the solution, the voluminous, white precipitate collected, and the operation repeated until no further deposit was formed. The solid was washed with much cold water, and appeared to be free from halogen. In order to free it from adhering alkali carbonate, it was boiled with water, but even after continued boiling it gave the flame reaction for sodium. This trace of impurity probably accounts for the low

percentages of carbon obtained in the analyses. It did not melt at 220° (Found: C=44·40, 44·16; H=3·01, 3·07; Bi=41·87, 41·45. $C_{19}H_{15}O_3Bi$ requires C=45·68; H=3·03; Bi=41·67 per cent.).

It is evident from these results that the compound which Michaelis described as a basic carbonate. $Ph_3BiO + CO_2$, is in reality the normal carbonate, Ph_3BiCO_3.

Triphenylbismuthine carbonate is insoluble in ordinary organic solvents; different preparations varied in colour from pure white to pale yellow. With concentrated hydrochloric acid, effervescence took place, and triphenylbismuthine dichloride (m. p. 126°) was obtained.

Action of Glacial Acetic Acid on Triphenylbismuthine Carbonate.

Three grams of triphenylbismuthine carbonate were dissolved in a small quantity of glacial acetic acid by the aid of heat. Carbon dioxide was evolved, and, on cooling and adding a small quantity of water, a white precipitate was obtained, which was collected and washed with light petroleum, air being drawn through until the solid no longer had the odour of acetic acid. The substance melted sharply at 162°, and on crystallisation from water and acetic acid had the same melting point. The yield was 3·3 grams (Found: C=47·06, 47·58; H=3·86, 3·72; Bi=37·31, 37·13. $C_{22}H_{21}O_4Bi$ requires C=47·39; H=3·79; Bi=37·32 per cent.).

Triphenylbismuthine acetate is a white powder completely soluble in glacial acetic acid or ethyl acetate on warming. It is readily soluble in cold chloroform or nitrobenzene and in xylene on warming, moderately so in warm benzene, acetone, carbon tetrachloride, or alcohol, and insoluble in water or light petroleum.

If the acetic acid solution of the acetate is allowed to remain for several days without addition of water, long, transparent needles separate, which soften at 130° and melt at 136—137° (Found: Bi=35·16, 35·36. $C_{22}H_{21}O_4Bi,\frac{1}{2}C_2H_4O_2$ requires Bi=35·43 per cent.).

If this substance is triturated with water, the acetate (m. p. 162°) is obtained, which, if dissolved in acetic acid and allowed to crystallise, again yields the acid acetate.

Action of Hydriodic Acid and Iodine on Triphenylbismuthine Carbonate.

Hydriodic acid, containing as usual a little free iodine, was added to the carbonate; a red compound was immediately formed and an odour of iodobenzene noticed. The red product appeared to be a mixture.

The same result was obtained when the carbonate was triturated with an aqueous solution of iodine.

Action of Sulphuric Acid on Triphenylbismuthine Dichloride.

Triphenylbismuthine dichloride (6 grams) was added during fifteen minutes, with constant shaking, to 20 c.c. of sulphuric acid maintained at about 10° Hydrogen chloride was evolved, and a clear solution obtained, through which air was drawn for three hours to remove dissolved hydrogen chloride, after which the mixture was poured on ice. The precipitated solid (5·3 grams) was well washed with water, dried, extracted twice with boiling chloroform, and washed with ether. The acid wash waters contained inorganic bismuth, from which, however, the solid was free (Found: Bi = 38·60; S = 6·10. $C_{18}H_{15}O_4SBi$ requires Bi = 38·80; S = 5·98 per cent.).

Triphenylbismuthine sulphate is a white solid not melting below 280°, and is very sparingly soluble in the usual organic solvents.

Action of Moist Ammonia Gas on Triphenylbismuthine Dichloride.

Nine grams of triphenylbismuthine dichloride were dissolved in chloroform containing a little light petroleum. Moist ammonia gas was passed in, the solution became cloudy, and soon deposited a white solid. This was collected, and the operation repeated until no more solid separated. The deposit was washed with cold water until all ammonium chloride was removed. Washing was then continued with boiling water. This produced violent frothing of the solid, and chloroform was evolved, the latter probably being present as chloroform of crystallisation. When no further effervescence was noticed, the residue was dried on porous porcelain, and then in the air. It melted at 156—158°, and, after crystallisation at 160—161°, the latter figure being unaltered after repeated recrystallisation. Two separate preparations were analysed (Found: Cl = 7·25, 7·20; Bi = 42·34, 42·54. $C_{18}H_{16}OClBi$ requires Cl = 7·21; Bi = 42·31 per cent.).

Triphenylbismuthine hydroxychloride is a white powder insoluble in water or light petroleum, moderately soluble in ether, acetone, benzene, or xylene, completely so in alcohol or nitrobenzene on heating, and readily so in cold chloroform.

The derivative containing chloroform was not analysed, since the combined solvent was liberated on keeping in air or drying in a vacuum.

Action of Sodium on Triphenylbismuthine Dichloride in Ether.

Five grams of triphenylbismuthine dichloride and 1 gram of sodium were suspended in ether and heated on a water-bath for nine hours, and the product was filtered. The filtrate, on keeping, deposited crystals melting at 160—162°, which did not depress the melting point of triphenylbismuthine hydroxychloride. The sodium in the residue was destroyed by alcohol, and the remaining solid extracted with acetone, when sodium chloride was left, and the solution gave a further quantity of hydroxychloride. The production of this compound was probably due to a trace of moisture in the ether.

Action of Water on Triphenylbismuthine Dichloride.

Two grams of triphenylbismuthine dichloride were dissolved in alcohol, the solution was poured into a large excess of water, and evaporated slowly to dryness. The residue was evaporated with water several times, and the melting point of the product was unchanged. No hydroxychloride, hydroxide, or oxide had thus been formed.

Action of Glacial Acetic Acid on Triphenylbismuthine Hydroxychloride.

Two grams of triphenylbismuthine hydroxychloride were dissolved in glacial acetic acid by the aid of heat. On cooling, a solid was deposited, which melted sharply at 142°. This was boiled with acetone and filtered. On cooling the filtrate, crystals appeared (m. p. 152—153°), containing bismuth and organic matter, but no halogen. Recrystallisation from chloroform and then alcohol gave products melting at 146—148° and 152—153°, probably impure triphenylbismuthine acetate (m. p. 162°).

The acetone mother liquors deposited well-defined crystals melting at 128—130° after recrystallisation from alcohol. Further crystallisation gave long needles (m. p. 126°), which did not depress the melting point of triphenylbismuthine dichloride.

The residue left from the acetone extraction of the product, melting at 142°, fused at 136—138°, and was shaken with cold chloroform, in which it was completely soluble. This solution was carefully investigated, but only unchanged basic chloride (m. p. 160—161°) and a small amount of a viscid residue could be isolated.

Action of Magnesium Methyl Iodide on Triphenylbismuthine Hydroxychloride.

Triphenylbismuthine hydroxychloride (1·2 grams) was added to a solution of 0·05 gram of magnesium and 0·3 gram of methyl iodide in dry ether; an orange coloration appeared, which persisted for some time. Next day the mixture was heated on a water-bath for five hours and filtered. The residue contained practically no organic matter. The main ethereal solution was evaporated, when two distinct types of crystals separated, together with a trace of oil. The crystals were washed with warm alcohol; the residue contained halogen, melted at 125—126°, and did not depress the melting point of triphenylbismuthine dichloride. The alcoholic solution yielded triphenylbismuthine. Since no trace of the iodine was discovered, it was probably contained in the oil, which was too small in quantity for further investigation.

Action of Moist Ammonia Gas on Triphenylbismuthine Dibromide.

The preparation was carried out as in the case of the basic chloride, the crude product apparently containing chloroform of crystallisation, as before. After washing with hot water, it melted at 150—151°, and, after four recrystallisations, had a constant melting point of 147—148° (Found: Br = 15·44, 15·41; Bi = 38·43, 39·13. $C_{18}H_{16}OBrBi$ requires Br = 14·91; Bi = 38·79 per cent.).

The two preparations were made at an interval of several months, and the somewhat high halogen content seems to point to the presence of a trace of unchanged dibromide.

Triphenylbismuthine hydroxybromide is a yellow powder, insoluble in water, light petroleum, or ether, sparingly soluble in boiling acetone or benzene, moderately so in boiling toluene or xylene, and readily so in boiling alcohol or nitrobenzene and in cold chloroform.

Action of Copper Bronze on Triphenylbismuthine Dichloride.

Five grams of triphenylbismuthine dichloride and 0·6 gram of copper bronze were heated for eleven hours with dry acetone on a water-bath, and the solid was separated. On treatment of the concentrated acetone solution with light petroleum, triphenylbismuthine, a small amount of copper chloride, and diphenylchlorobismuthine (2·4 grams: m. p. 184—186°) were obtained whilst the final residues had a strong odour of chlorobenzene

The last two substances were probably formed from the dichloride by the prolonged heating, and not owing to the action of the copper.

Molecular Weights of some Bismuth and Arsenic Derivatives.

These determinations were carried out by the cryoscopic method in benzene solution.

Triphenylbismuthine.—0·2845 gave $\Delta = -0·153°$. M.W. 427. $(C_6H_5)_3Bi$ requires 439.

Triphenylarsine.—0·2370 gave $\Delta = -0·179°$. M.W. 298·9. $(C_6H_5)_3As$ requires 306·1.

Tri-p-*tolylbismuthine.*—0·2304 gave $\Delta = -0·115°$. M.W. 458·3. $(C_7H_7)_3Bi$ requires 481.

Tri-p-*tolylarsine.*—0·3605 gave $\Delta = -0·241°$. M.W. 342·8. $(C_7H_7)_3As$ requires 348.

Triphenylbismuthine Dichloride.—0·8847 gave $\Delta = -0·470°$. M.W. 498·5. $(C_6H_5)_3BiCl_2$ requires 509·5.

Tri-α-naphthylbismuthine.—0·1588 gave $\Delta = -0·122°$. M.W. 577. $(C_{10}H_7)_3Bi$ requires 589.

All the above show normal values.

Action of Magnesium p-*Tolyl Bromide on Triphenylbismuthine Dichloride.*

The Grignard solution (1·1 mols.) was added to triphenylbismuthine dichloride suspended in ether, and the usual transient violet coloration observed. The whole was heated on a water-bath for three to four hours, when a granular precipitate settled out. After twelve hours, the ether was evaporated and the residue distilled in a current of steam. The product remaining in the distillation flask solidified (m. p. 72—73°), and was recrystallised four times from alcohol, giving crops melting at 76°, 78°, 78°, the last fraction being melted with triphenylbismuthine. The mother liquors were fractionally crystallised, but no product other than triphenylbismuthine could be isolated.

Action of Magnesium p-*Tolyl Bromide on Diphenylbromobismuthine.*

The reaction was carried out as above, and the mixture distilled in a current of steam; the residue melted at 70°, and was recrystallised three times from acetone, but in each case the crystals melted at 78° and gave the reactions of triphenylbismuthine. The mother liquors yielded a further quantity of triphenylbismuthine.

Action of Iodine Trichloride on Triphenylbismuthine.

Five grams of the bismuthine were dissolved in dry ether and 2·7 grams of iodine trichloride in the same solvent gradually added. A momentary red coloration appeared on mixing, and a pale brown oil separated out and soon solidified. The ethereal solution was evaporated, yielding an oil, which with chlorine in chloroform solution gave 0·4 gram of iodobenzene dichloride. The solid, after crystallisation from acetone and light petroleum, melted at 120° and did not depress the melting point of triphenylbismuthine dichloride.

Tri-α-naphthylbismuthine Dichloride.

Five grams of the bismuthine were dissolved in dry chloroform and treated with chlorine. The addition of light petroleum gave a yellow precipitate (4·6 grams: m. p. 158—159°), and the mother liquors yielded a further 0·7 gram. Recrystallisation twice from chloroform–petroleum solution gave a product melting sharply on both occasions at 166° (Found: Cl=10·68, 10·66; Bi=30·67, 30·84. $C_{30}H_{21}Cl_2Bi$ requires Cl=10·74; Bi=31·51 per cent.).

Tri-α-naphthylbismuthine dichloride is a yellow, crystalline powder readily soluble in chloroform, moderately so in acetone or benzene, and insoluble in light petroleum. On heating for several hours at 100°, it did not smell of chloronaphthalene, was stable to hydrochloric acid, and melted at 167—169°.

Action of Moist Silver Oxide on Tri-α-naphthylbismuthine Dichloride.

The dichloride (2 grams) and silver oxide (0·7 gram) were suspended in moist acetone and well shaken. Reaction occurred almost at once, and, after two days, the mixture was filtered and the residue extracted with chloroform, which yielded two deposits of tri-α-naphthylbismuthine, 0·5 gram (m. p. 230°) and 0·2 gram (m. p. 232° on one crystallisation). Spontaneous evaporation of the acetone solution yielded a small amount of a brown solid, which became very viscid on warming with alcohol, had a strong odour of naphthalene, and was not further examined.

Diphenyl-α-naphthylbismuthine Dibromide.

Diphenyl-α-naphthylbismuthine (0·8 gram) was treated in dry chloroform–ether solution with a slight excess of bromine in chloro-

form. On addition of light petroleum, 0·81 gram of dibromide was precipitated (Found: Br = 24·83; Bi = 31·87. $C_{22}H_{17}Br_2Bi$ requires Br = 24·59; Bi = 31·99 per cent.).

Determination of the Metal in Derivatives of Quinquevalent Bismuth.

The substance (0·2—0·3 gram) was treated with about 10 c.c. of an ammoniacal solution of hydrogen sulphide, and the mixture evaporated to dryness in an air-bath at 115—125°, the benzene formed during the decomposition driven off, and the residue of bismuth sulphide and sulphur boiled for a few minutes with 10 c.c. of concentrated hydrochloric acid. The solution was filtered, diluted with water, hydrogen sulphide passed, and the precipitated bismuth sulphide filtered on a Gooch crucible, washed with carbon disulphide, dried, and weighed.

The method was first tested on two well-known compounds, namely, triphenylbismuthine dichloride (Found: Bi = 40·44. $C_{18}H_{15}Cl_2Bi$ requires Bi = 40·78 per cent.) and dibromide (Found: Bi = 34·92. $C_{18}H_{15}Br_2Bi$ requires Bi = 34·73 per cent.).

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THE UNIVERSITY,
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LXXXIII.—*Note on the Preparation of certain Iodo-compounds.*

By CUTHBERT WILLIAM JAMES, JAMES KENNER, and WILFRID VICTOR STUBBINGS.

THE authors, having occasion to attempt the preparation of certain 2:6-derivatives of iodobenzene from the corresponding amino-compounds, were confronted with the well-known difficulty that a number of the latter are only very incompletely diazotised under the conditions usually employed. The yield, however, of iodo-compound obtained was usually very satisfactory when allowance was made for the proportion of amino-derivative unchanged. It therefore only remained to achieve complete diazotisation, and it was decided to apply the process specially recommended by Witt

in such cases (*Ber.*, 1909, **42**, 2953), and consisting in the addition of a mixture of the base with a molecular proportion of potassium metabisulphite to fuming nitric acid. By pouring the product on ice, as described by Witt, and adding a solution of iodine in potassium iodide, extremely satisfactory yields of great purity were achieved in the cases of 2-iodo*iso*phthalic acid, 2-iodo-3-nitrobenzoic acid, and 5-chloro-4-iodo-3-nitrotoluene. 5-Iodo*iso*phthalic acid is more satisfactorily prepared by the ordinary process, which involves no difficulty as regards diazotisation. Attempts to prepare picryl iodide were unsuccessful, probably owing to instability of the diazonium compound, and the method is also obviously unsuitable for compounds like benzidine, which are easily nitrated.

When the diazotised solution, prepared by Witt's process from 3-nitroanthranilic acid, was added to a large excess of cuprous chloride solution, the product contained, besides the desired chloronitrobenzoic acid, a considerable amount of hydroxy-compound. Apparently, therefore, the method is unsuitable for the preparation of chloro-derivatives. For many purposes, however, iodo-compounds are at least equally suitable, and it was considered that the successful outcome of the experiments now described might more usefully be separately recorded than as an incident in the syntheses for which the compounds in question were required.

EXPERIMENTAL.

*2-Iodo*iso*phthalic Acid.*

The starting point for the preparation of this compound was 2-nitro-*m*-toluic acid. The oxidation of this compound to 2-nitro*iso*phthalic acid, referred to by Noelting and Gachot (*Ber.*, 1906, **39**, 73), by neutral potassium permanganate solution is only complete after the mixture has been boiled for some hours. Noelting and Gachot also describe the preparation of 2-amino*iso*phthalic acid from the nitro-acid by means of tin and hydrochloric acid; it is more conveniently carried out by the addition of stannous chloride to a suspension of the nitro-derivative in a boiling mixture of acetic and hydrochloric acids. The free amino-acid separates on cooling the solution.

The conversion of 2-amino*iso*phthalic acid into 2-iodo*iso*phthalic acid was carried out by Mayer (*Ber.*, 1911, **44**, 2301), but, as he admits, the product was very impure. On repeating the process, which consisted in the very slow addition of a solution of the sodium salt of the acid and of sodium nitrite to dilute sulphuric acid, a purer product was obtained, but only about 25 per cent. of the material was diazotised after thirty hours. Witt's process

was therefore adopted, a finely ground mixture of amino*iso*phthalic acid (20 grams) and potassium metabisulphite (12·5 grams) being gradually added to fuming nitric acid (45 c.c.) below 10°. After four hours, the mixture was poured on ice (220 grams), and to the resulting clear solution was added a solution of iodine (17 grams) in potassium iodide (33 grams) in the minimum quantity of water. The product (29 grams) melted at 229°. By crystallisation from water, the melting point rose to 236—238°, but a determination of the equivalent showed the acid still to contain 5 per cent. of hydroxy*iso*phthalic acid. Mayer gives a melting point of 205—222°, even after purification of the acid through its methyl ester. The probable explanation of the discrepancy became obvious when a small portion of the acid was submitted to hydrolysis by boiling alcoholic sodium hydroxide. As a result, pure hydroxy*iso*phthalic acid, $C_6H_3(OH)(CO_2H)_2,H_2O$ (m. p. 244°; equivalent, 99·3), was obtained, and further characterised by its red coloration with ferric chloride.

3-*Nitroanthranilic Acid.*

3-Nitroaceto-*o*-toluidide was easily obtained by the addition of sulphuric acid (2 grams) to a mixture of 3-nitro-*o*-toluidine (20 grams) and acetic anhydride (26 grams). A clear solution resulted, accompanied by a rise in temperature to 70°, and almost immediately after the whole set to a mass of crystals, which were collected after the addition of water. The product (25·5 grams) melted at 156°, which was raised to 157—158° by recrystallisation from dilute acetic acid.

3-Nitroacetylanthranilic acid was prepared by oxidising 3-nitroaceto-*o*-toluidide (10 grams) at 100° with a solution of potassium permanganate (22 grams) and magnesium sulphate (16 grams) in water (1100 grams). For some unexplained reason, the melting point of the product (9 grams) varied considerably. By fractional crystallisation from dilute acetic acid, the product of several preparations was separated into two distinct substances, one in the form of stout, golden-yellow prisms (m. p. 244·5°), the other in yellow needles (m. p. 178°), which it is hoped to discuss in a subsequent communication.

By boiling 3-nitroacetylanthranilic acid, either the crude oxidation product or the separate compounds above described, for thirty-five minutes with 50 per cent. sulphuric acid (4 parts), almost pure 3-nitroanthranilic acid (m. p. 205°) is obtained in a yield of more than 90 per cent. The yield is diminished if the strength of acid or the duration of boiling is increased. The acid has been previously described by Hübner (*Annalen*, 1879, **195**,

37), who obtained it in the form of its ester by the action of ammonia on ethyl 3-nitrosalicylate.

It is noteworthy that the esterification of the acid is only accomplished with difficulty under ordinary conditions. Thus, after the acid (10 grams) had been boiled with alcohol (50 c.c.) and sulphuric acid (5 c.c.) for twenty-four hours, 5 grams remained unchanged, and 5·8 grams of ester had been produced.

2-Iodo-3-nitrobenzoic Acid.

(*a*) When a suspension of 3-nitroanthranilic acid (10 grams) in sulphuric acid (11 grams) and water (53 grams) was diazotised in the usual manner, 5·5 grams of acid remained undissolved, whilst from the solution 7 grams of crude iodonitrobenzoic acid were obtained. A similar, but less satisfactory, result was obtained when the ester was used in place of the free acid.

(*b*) 202·5 Grams of nitrobenzoic acid, when submitted to the treatment already described in the case of amino*iso*phthalic acid, gave 321 grams of iodonitrobenzoic acid (m. p. 203—206°), a yield of 98 per cent. of the theoretical.

By crystallisation from water, the acid is obtained in prisms melting at 206° (Found: N = 4·82. $C_7H_4O_4NI$ requires N = 4·78 per cent.).

5-Chloro-4-iodo-3-nitrotoluene.

(*a*) In an experiment by Mr. C. W. Judd, from 15 grams of 5-chloro-3-nitro-*p*-toluidine, which had been treated with nitrous acid and potassium iodide in the usual manner, 9 grams were recovered unchanged, whilst 6·5 grams of chloroiodonitrotoluene (m. p. 83°) were generated from the remainder.

(*b*) Three grams of the base, treated as described for 2-amino*iso*phthalic acid, gave 3·7 grams of iodo-derivative (m. p. 92°).

5-Chloro-4-iodo-3-nitrotoluene separates from light petroleum in plates melting at 92°, which are colourless when pure, but usually red (Found: N = 4·85. $C_7H_5O_2NClI$ requires N = 4·71 per cent.).

The authors wish to express their acknowledgments to the Research Fund Committee of the Chemical Society for a grant, to The British Dyestuffs Corporation for supplies of *o*-toluidine, and to Messrs. Whiffen and Sons for the iodide used in these experiments. Two of them (C. W. J. and W. V. S.) also wish to thank the Corporation for the opportunity of collaborating in this work.

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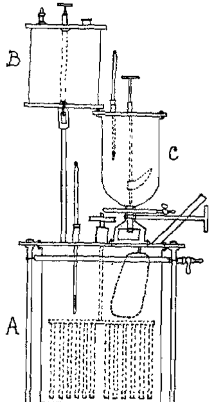
LXXXIV.—*Diphenylarsenious Chloride and Cyanide.* (*Diphenylchloroarsine and Diphenylcyanoarsine.*)

By Gilbert T. Morgan and Dudley Cloete Vining.

The employment of diphenylarsenious chloride as a military poison has led in recent years to many experiments on the preparation of this compound and its intermediates.

In one of these processes, triphenylarsine is the starting point, and this intermediate is produced by Michaelis's modification of the Fittig reaction, in which arsenious chloride, chlorobenzene, and sodium interact in an inert medium (La Coste and Michaelis, *Ber.*, 1878, **11**, 1881; *Annalen*, 1880, **201**, 215; 1881, **207**, 195; 1902, **321**, 160; Philips, *Ber.*, 1886, **19**, 1031). As practised by these investigators, the process is unsuitable for large-scale operations. The introduction of the whole of the sodium at the commencement of the process renders the operation hard to regulate, and unless great care is taken, the condition of the metal as regards superficial oxidation is likely to vary considerably from one batch to another, so that the onset and course of the reaction are not easily controlled. Moreover, the sludgy form in which the sodium chloride is left at the end of the condensation when carried out under the earlier laboratory conditions leads to further difficulties in the separation of triphenylarsine. The sodium present in large excess at the commencement of the operation certainly sets up side reactions, leading to the formation of diphenyl and ill-defined arsenical products. In the small-scale plant illustrated in Fig. 1, these difficulties were obviated, and the whole operation could be completed without the addition of water, another factor which makes for safety.

Fig. 1.



The cylindrical, steel reaction vessel (3 litres capacity), fitted

with a steel cover rendered gas-tight with an asbestos washer, was supported by four upright steel rods fixed in a trough with a waste-pipe leading to the sink. Round the outside of the reaction vessel, and near the top, a perforated water-pipe was carried concentrically, and attached to the steel supports. By this means, a stream of cold water could be distributed over the outer surface of the reaction vessel, which could also be heated by a rose burner.

The cover of the reaction vessel, *A*, which was perforated to admit a thermometer, carried the following fittings:

(1) A central steel comb stirrer provided with a pulley for mechanical stirring.

(2) A water-cooled steel reflux condenser.

(3) A baffle plate projecting into the vessel to assist in the mixing of the contents and to prevent the rotating liquid from splashing up in the condenser.

(4) A sodium dropping apparatus, *C*, consisting of a cylindrical steel container (1 litre capacity) with a curved bottom perforated at its lowest point with an outlet hole (0·6 cm. in diameter). A steel tap and a sight-feed with transparent silica windows attached to the base of the container enabled the operator to regulate the flow of molten sodium.

A ring burner placed under the base of the sodium container just above the outlet tap was used to keep the metal in a molten condition. The steel cover of the container, made air-tight with an asbestos washer, carried a thermometer and a hand stirrer, shaped to scour the bottom of the container and provided with a sharp prong to dislodge any obstacle in the outlet tap.

(5) A cylindrical glass reservoir, *B*, for liquid (capacity, 800 c.c.) with steel ends, fitted with vertical outlet tube to reaction vessel, a needle valve regulated by a spindle, and a sight-feed with glass window. The steel cover of this reservoir was fitted with a screw-stoppered inlet and with a valve for introducing compressed air, so that the contained liquid was expelled under slight pressure.

Procedure.—Arsenious chloride (276 grams), chlorobenzene (510 grams), and xylene (400 c.c.) were mixed; half the liquid was placed in the reservoir and half in the reaction vessel, where it was diluted with 800 c.c. of xylene. Sodium (210 grams) was introduced into the sodium container and covered with xylene. The reaction vessel was heated to 70° and the sodium container to 110°. Stirring was commenced (speed of rotation, 250—300 revs. per minute), the sight-feed of the sodium apparatus warmed with a Bunsen burner, and molten sodium dropped into the reaction vessel, the rate being regulated by the lower thermometer, the

temperature of which was not allowed to rise above 70°. External cooling was applied when necessary.

After fifteen minutes, the solution from the liquid reservoir was allowed to flow in concurrently with the molten sodium. When all the reagents had been introduced, stirring was continued until the temperature began to fall without external cooling by water. The reaction vessel was then heated to 90° and allowed to cool. At 60° the mixture was filtered through a Bornett press, the granular precipitate of sodium chloride was washed with warm xylene, and afterwards exposed to the atmosphere until any traces of unaltered sodium had been oxidised. The filtrate was distilled up to 220° to remove solvent and chlorobenzene. The liquid residue, on cooling, changed to a pale yellow, crystalline mass of triphenylarsine (m. p. 58—59°). Yield, 383 grams=82 per cent.

The outstanding advantages of this process are as follows:

(1) As sodium is never in excess during the reaction, the process is readily controlled.

(2) Water is excluded from all stages of the preparation, thus eliminating danger from the explosive interaction of sodium and this liquid.

(3) The salt residue is granular and easily filtered.

(4) The product is obtained directly in a state of purity without further treatment.

(5) Other coal-tar hydrocarbons, such as benzene or toluene, can be substituted for xylene as the working fluid in this plant without any material change in the procedure.

(6) The foregoing apparatus can be employed with advantage for other applications of the Fittig reaction, the gradual addition of clean, unoxidised sodium being a useful improvement on the older processes.

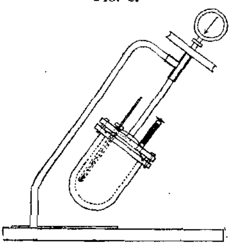
Very favourable results were obtained in the preparation of triphenylstibine. Freshly distilled antimony trichloride (344 grams), chlorobenzene (510 grams), and xylene (400 c.c.) were mixed, and the solution was divided equally between reservoir and reaction vessel. In the latter case, 600 c.c. of xylene were added as diluent. Sodium (210 grams) covered with 500 c.c. of xylene was placed in the sodium container, and the process effected at 70° in the manner already described. After filtering off in the Bornett press the dark grey, granular sodium chloride, the filtrate, on distilling up to 220°, left a residue of triphenylstibine (m. p. 48—50°).

The Rotating Autoclave.

I. *Conversion of Triphenylarsine into Diphenylarsenious Chloride.*

This conversion was carried out in the rotating autoclave, a vessel formed by boring out the steel core of a 6-inch high-explosive shell until the thickness of the wall was about 1·9 cm. The steel cover, which was of similar thickness, was fastened down with twelve bolts and rendered gas-tight with a lead washer. The cover carried a powerful adjustable spring safety valve, a steel thermometer tube projecting into the cavity of the autoclave, and a hollow steel tube carrying an all-steel pressure gauge, which communicated with the interior of the vessel by means of a narrow, bored steel tube dipping into and protected by a concentric steel case partly filled with heavy oil, and having a small aperture at its upper end for admitting the compressed gases from the autoclave. The pressure-gauge tube was fixed in the centre of the cover and fitted with a pulley, so that it also served as the axle of rotation for the autoclave, which was supported and spun in an inclined position. Rotating autoclaves have been made on these lines by Mr. H. Edenborough, of the Technical College, Finsbury, with capacities ranging from 500 c.c. to 9 litres.

FIG. 2.



The vessel used in the following experiments had a working capacity of 1 litre. A glass lining blown to fit into the cavity of the autoclave was employed in lieu of an enamelled lining.

Procedure.—Triphenylarsine (250 grams) was heated for three hours with 75 grams of arsenious chloride at 250—280°, the pressure attained being about 4·2—7 kilos. per sq. cm. The contents of the autoclave were then distilled in a current of carbon dioxide under a pressure of 20—30 mm., the following fractions being collected:

(*a*) 150—190°: 68 grams, consisting of phenylarsenious dichloride with 32 per cent. of diphenylarsenious chloride.

(*b*) 190—220°: 180 grams of diphenylarsenious chloride, 93 per cent.

(*c*) 220—250°: 7 grams of triphenylarsine with 30 per cent. of diphenylarsenious chloride.

(*d*) Residue in still when extracted with chloroform yielded 27 grams of unchanged triphenylarsine.

Fraction (*b*) was cooled and drained, when it yielded 155 grams of colourless, crystalline diphenylarsenious chloride (m. p. 39—40°). The total yield of diphenylarsenious chloride was 66 per cent., of which 53 per cent. was isolated in a state of purity.

Fractions (*a*) and (*c*) and the triphenylarsine extracted from (*d*) were heated to 150° to remove volatile impurities, and returned to the autoclave for a subsequent operation, when 60 per cent. of this material was converted into crystalline diphenylarsenious chloride.

The residues from the second operation were available for further treatment, and the total yield of diphenylarsenious chloride was correspondingly increased. It was also found that 25 per cent. of this product could be frozen out from the contents of the autoclave without distillation.

By the foregoing dry processes, chlorobenzene and arsenious chloride can be converted into crystalline diphenylarsenious chloride without the intervention of water or the use of any aqueous reagent, the overall yield of this product being upwards of 60 per cent.

II. *Diphenylarsenious Chloride from Phenylarsenious Dichloride.*

The foregoing operations showed that the rotating autoclave can also be used with advantage in producing diphenylarsenious chloride from triphenylarsine obtained by the dry process, and phenylarsenious dichloride prepared by Bart's *diazo*-process (D.R.-P. 250264; Chem. Fabrik. von Heyden, D.R.-P. 264924).

These two reagents when heated for three hours at 250—280° gave a 60 per cent. yield of diphenylarsenious chloride, separated by the above-described fractional distillation.

III. *Diphenylstibine Chloride.*

Triphenylstibine, when heated with redistilled antimony trichloride for three hours at 250—280° in this autoclave, was converted into a mixture of diphenylstibine chloride (m. p. 68—70°) and phenylstibine dichloride (Morgan and Micklethwait, T., 1911, **99**, 2295).

IV. *Diphenylarsenious Cyanide.*

(1) *From Diphenylarsenious Oxide.*—Diphenylarsenious oxide immersed in pure anhydrous hydrogen cyanide and left in contact with excess of this reagent for twenty-four hours yielded a yellow

oil which, on seeding with crystals of diphenylarsenious cyanide, solidified to a crystalline solid melting at 28—30° (Sturniolo and Bellinzoni, *Boll. chim. farm.*, 1919, **58**, 409, give m. p. 35°); this product contained 84 per cent. of diphenylarsenious cyanide and 12 per cent. of diphenylarsenious oxide. A similar experiment carried out with 90 per cent. hydrogen cyanide gave a product melting at 29—30°, and containing 87·5 per cent. of diphenylarsenious cyanide.

It was next found that it was quite unnecessary to work with anhydrous hydrogen cyanide in order to obtain diphenylarsenious cyanide. The following three methods, which are based on the use of cyanides of the heavy metals, rendered it possible to dispense entirely with concentrated aqueous solutions of hydrogen cyanide or its alkali salts.

(2) *From Diphenylcacodyl.*—Diphenylarsenious chloride (53 grams) was stirred at 100° with 30 c.c. of commercial hypophosphorous acid (30 per cent.). Diphenylcacodyl (tetraphenyldiarsine) separated in a yield of 83 per cent. This product was heated at 250° with mercuric cyanide in the rotating autoclave in the proportions demanded by the following equation:

$$Ph_2As{\cdot}AsPh_2 + Hg(CN)_2 = 2Ph_2As{\cdot}CN + Hg.$$

The organic product was extracted with benzene, and the yield of diphenylarsenious cyanide was 94 per cent. of the calculated amount.

A similar experiment was carried out with silver cyanide, according to the equation

$$Ph_2As{\cdot}AsPh_2 + 2AgCN = 2Ph_2As{\cdot}CN + 2Ag.$$

The result obtained was not so satisfactory.

(3) *From Diphenylarsenious Sulphide.*—Diphenylarsenious chloride was dissolved in benzene and shaken for fifteen minutes with a saturated aqueous solution of sodium sulphide ($1\frac{1}{4}$ mols.). The benzene solution, washed with water, dried with anhydrous calcium chloride, and concentrated, yielded a mass of colourless needles of diphenylarsenious sulphide; yield, 93 per cent. After one recrystallisation, the substance melted at 64°.

The foregoing sulphide was mixed with mercuric cyanide in the following proportions and heated for two hours at 160—200°:

$$Ph_2As{\cdot}S{\cdot}AsPh_2 + Hg(CN)_2 = 2Ph_2As{\cdot}CN + HgS.$$

The organic product was separated from mercuric sulphide with benzene, the yield of diphenylarsenious cyanide being 71 per

Experiments were also carried out, using silver cyanide, according to the equation

$$Ph_2As{\cdot}S{\cdot}AsPh_2 + 2AgCN = 2Ph_2As{\cdot}CN + Ag_2S.$$

The temperature was kept at 160° and the product extracted with dry benzene as before, the yield of diphenylarsenious cyanide being 69 per cent.

(4) *From Diphenylarsenious Chloride.*—After preliminary experiments, the following method was adopted in the preparation of 7½ kilos. of dry, alkali-free diphenylarsenious cyanide. Silver cyanide was prepared quantitatively from silver nitrate by precipitation with a dilute aqueous solution of hydrogen cyanide and dried at 120°.

Diphenylarsenious chloride was heated with a 10 per cent. excess of dry silver cyanide in the glass-lined rotating autoclave for three hours at 150—160°. The contents of the autoclave were allowed to cool to 40°, and filtered through a heated filtering apparatus. When the liquid had been thoroughly drained from the silver chloride, the latter was extracted with warm, dry benzene, and the clear solution distilled. The total yield of diphenylarsenious cyanide was about 92 per cent. of the calculated amount. The product, without further purification, melted at 28°, and contained 90 per cent. of the cyanide, the remaining 10 per cent. consisting of diphenylarsenious oxide and chloride.

In this operation, 5 kilos. of silver cyanide were employed, and, after washing with hot benzene until free from organic arsenicals, the residual silver chloride was reduced to silver by fusion with sodium carbonate. Even with an improvised smelting apparatus, the total loss of this metal was less than 2 per cent.

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Finsbury, London, E.C.2. [*Received, May 15th, 1920.*]

LXXXV.—*ortho-Chlorodinitrotoluenes. Part I.*

By Gilbert T. Morgan and Harry Dugald Keith Drew.

The direct nitration of *o*-chlorotoluene as carried out by Nietzki and Rehe (*Ber.*, 1892, **25**, 3005) resulted in the isolation of one dinitro-compound, 2-chloro-3:5-dinitrotoluene. Further nitration of the 3- and 5-nitro-derivatives of *o*-chlorotoluene by Borsche and Fiedler led to the same dinitro-compound, these investigators indicating a melting point of 63—64°, whereas the earlier workers gave it as 45° (compare Rabaut, *Bull. Soc. chim.*, 1895, [iii], **13**, 634, and Körner and Contardi, *Atti R. Accad. Lincei*, 1915, [v], **24**, i, 888).

Another dinitro-compound (m. p. 106—107°) was obtained by Jansen (D.R.-P. 107505) on nitrating 2-chloro-6-nitrotoluene (compare Cohn, *Monatsh.*, 1901, **22**, 475).

In the research described below, the nitration of *o*-chlorotoluene to dinitro-derivatives has been investigated more completely, and two new isomerides are described and identified as the 4:5- and 4:6-dinitro-compounds.

Nitration of o-Chlorotoluene.

Eighty grams of *o*-chlorotoluene (I) were added during two hours to 400 c.c. of concentrated sulphuric acid and 160 c.c. of nitric acid (D 1·42) at 8—10°, the mixture being afterwards heated for four hours on the water-bath. The yellow, supernatant oil from three batches weighed 340 grams, and the spent acids, poured on to ice, gave an additional 36 grams (total yield, 91·5 per cent. of the theoretical).

The oily product partly solidified on cooling, and the solid portion, when crystallised from alcohol, yielded pure 2-chloro-3:5-dinitrotoluene (V); the alcoholic filtrate gave mixed crystals of this compound (m. p. 64°) and of the 5:6-isomeride (m. p 101—106°). As a satisfactory separation of these two products could not be effected by alcohol, petroleum, benzene, or acetic acid, recourse was had to crystallisation from concentrated sulphuric acid, a method formerly employed by Crossley and Renouf in separating the dinitro-*o*-xylenes (T., 1909, **95**, 202). The oily mixture (340 grams) was dissolved in 800 c.c. of concentrated sulphuric acid on the water-bath, and this solution yielded, on cooling, 43 grams of crystalline material, which, on fractional crystallisation from alcohol, gave 30 grams of the 5:6-dinitro-compound, 3 grams of the more soluble 4:5-isomeride (m. p. 87—88°), and 10 grams of an intimate mixture (m. p. 63—65°) of these two

isomeric compounds. The mixture contains the 4:5- and 5:6-*isomerides* in the proportions, respectively, of 2:1, and as this ratio represents their relative solubilities in alcohol, they are not readily separated from the mixture by the use of this solvent.

The concentrated acid filtrate, when treated with ice, gave 100 grams of crystals and 152 grams of oil. The solid part, when crystallised successively from concentrated sulphuric acid and alcohol, furnished a mixture of the 3:5- and 4:5-isomerides, the former predominating. The oily portion on similar treatment was fractionated chiefly into the same pair of isomerides and a small amount of the intimate mixture of the 4:5- and 5:6-isomerides.

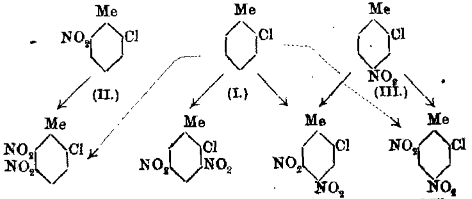
The process of crystallisation from concentrated sulphuric acid was repeated many times on the more fusible fractions melting below 50°. The two *o*-dinitro-compounds, the 4:5- and 5:6-isomerides, are less soluble in cold concentrated sulphuric acid than the *m*-dinitro-compounds, the 3:5- and 4:6-isomerides. Hence the former pair gradually accumulated in the crystalline fractions, whilst the latter became concentrated in the acid filtrate.

As the result of a lengthy, systematic fractionation, 340 grams of crude nitration product yielded 125 grams of the 3:5-*dinitro-compound*, 30 grams of the 5:6-isomeride, 15 grams of the 4:5-compound, and 63 grams of the intimate mixture (m. p. 63—65°) of the last two substances. The oily material obtained from the final filtrates, which consisted largely of impure 3:5-compound, gave the reactions of the 4:6-isomeride (m. p. 49°).

The 4:5- and 4:6-dinitro-compounds have been obtained more readily by the nitration of 2-chloro-4-nitrotoluene (p. 786), and further nitration of 2-chloro-6-nitrotoluene has given as the *main product* the 5:6-*dinitro-compound* (p. 787).

The solubilities in concentrated sulphuric acid or in methyl or ethyl alcohol of the three isomerides containing the nitro-groups in positions 3:5-, 4:5-, and 5:6- are respectively in the ratio 4:2:1.

The diagram below illustrates the derivation of the four



(IV.) (V.) (VI.) (VII.)

2-chlorodinitrotoluenes either directly from *o*-chlorotoluene or indirectly from 4- and 6-nitro-2-chlorotoluenes.

Nitration of 2-Chloro-4-nitrotoluene.

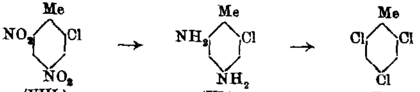
2-Chloro-4:5-dinitrotoluene (VI).—2-Chloro-4-nitrotoluene (III) (51 grams) was added slowly to 250 c.c. of concentrated sulphuric acid and 60 c.c. of nitric acid (D 1·42), the temperature being maintained at 40—45° for one hour. The mixture was then heated to 90° until the characteristic odour of the mononitro-compound had disappeared. When crystallised from alcohol, the nitration product yielded 49 grams of pure 2-chloro-4:5-dinitrotoluene melting at 88·5°, the yield being upwards of 85 per cent. (Found: Cl = 16·58; N = 13·15. $C_7H_5O_4N_2Cl$ requires Cl = 16·37; N = 12·93 per cent.).

2-Chloro-4:5-dinitrotoluene separated from cold alcohol in lustrous, colourless, hexagonal leaflets, or in tough, prismatic needles at higher temperatures.

2-Chloro-4:6-dinitrotoluene (VII).—The oily residue from the foregoing 4:5-dinitro-compound was subjected to fractional crystallisation from concentrated sulphuric acid in order to separate the other isomeride. The crystallising fraction consisted of nearly pure 4:5-dinitro-compound, whilst the acid filtrate yielded on dilution with water crystals of *2-chloro-4:6-dinitrotoluene* (m. p. 49°) and an oily mixture of the two isomerides. Repeated fractionation of this oil in concentrated sulphuric acid led to the gradual separation of the two constituents. The total yield of the 4:6-compound was about 12 per cent., of which half was isolated in a state of purity (Fouud: Cl = 16·39; N = 13·09. $C_7H_5O_4N_2Cl$ requires Cl = 16·37; N = 12·93 per cent.).

2-Chloro-4:6-dinitrotoluene is very soluble in alcohol, and crystallises in colourless, rectangular prisms or in prismatic needles. Like its isomerides, it is odourless. It does not react with aniline in boiling benzene, but with liquid or alcoholic ammonia it gives rise to ill-defined, shellac-like products.

With zinc dust, ammonium chloride, and dilute alcohol, or with alcoholic stannous chloride and hydrochloric acid, the 4:6-dinitro-compound underwent reduction to *6-chloro-2:4-tolylenediamine* (IX), crystallising from benzene or from alcohol and water in needles melting at 69·5°. With diazonium salts, this base gave the reactions of a meta-diamine; its constitution was determined by converting it, through the Sandmeyer reaction, into 2:4:6-trichlorotoluene (X), melting at 33—34° (Cohen and Dakin, T., 1902, **81**, 1335).



(VIII.) (IX.) (X.)

Nitration of 2-Chloro-6-nitrotoluene.

2-Chloro-5:6-dinitrotoluene (IV).—A specimen of 6-nitro-*o*-toluidine, available through the kindness of Prof. Green, was converted by the Sandmeyer reaction into 2-chloro-6-nitrotoluene (*II*) (m. p. 36—37°), and the latter compound nitrated at 20° with 15 parts of concentrated sulphuric acid and 2 parts of nitric acid (D 1·42), the reaction being completed at 80°. The yield of 5:6-dinitro-compound was upwards of 85 per cent., and there was a small amount of oily by-product. 2-Chloro-5:6-dinitrotoluene melting at 106·5° separated from methyl or ethyl alcohol in colourless needles or prisms; its constitution was confirmed by the following processes.

Action of Ammonia on 2-Chloro-5:6-dinitrotoluene.—When treated either with liquefied ammonia or with saturated alcoholic ammonia, 2-chloro-5:6-dinitrotoluene was converted quantitatively into 6-chloro-3-nitro-*o*-toluidine, the inorganic product being ammonium nitrite entirely free from ammonium chloride. On crystallising from alcohol, the nitroamine separated in pale amber, highly refractive prisms with pyramidal ends; it melted at 151·5° and had a faint vanilla odour (*Found*: Cl=19·18; N=15·18. $C_7H_7O_2N_2Cl$ requires Cl=19·01; N=15·02 per cent.).

6-Chloro-3-nitro-o-toluidine (XII), which was only very sparingly soluble in water, dissolved more readily in warm, moderately concentrated acid, ether, or the alcohols. It was not benzoylated under Schotten-Baumann conditions.

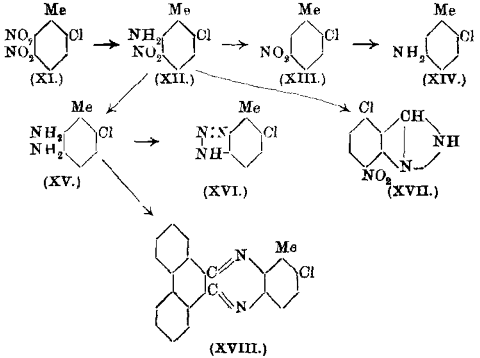
4-Chloro-7-nitroindazole (XVII).—A solution of the diazonium sulphate of the foregoing nitroamine (1·6 grams) was boiled with alcohol, and the product distilled in a current of steam, when the distillate contained 2-chloro-6-nitrotoluene (0·8 gram), and the residue yielded a voluminous mass of felted, yellow needles (0·6 gram), very sparingly soluble in hot water, crystallising from warm alcohol, and dissolving in aqueous sodium hydroxide to a bright yellow solution (Found: N=21·49; Cl=17·93. $C_7H_4O_2N_3Cl$ requires N=21·28; Cl=17·95 per cent.). This indazole melted at 218°, and, on warming, had a marked odour resembling that of iodoform.

The foregoing 2-chloro-6-nitrotoluene (XIII) was characterised

by conversion into 6-chloro-*m*-toluidine (XIV) and its benzoyl derivative, these compounds melting respectively at 84° and 119—120° (Wibaut, *Rec. trav. chim.*, 1913, **32**, 244).

These results show that it is the 6-*nitro*-group which is displaced quantitatively by the amino-radicle. This displacement was unexpected, inasmuch as it was to be anticipated that the 5-nitro-group would be the most mobile of the three acidic substituents, owing to its position in regard to the chlorine atom and the other nitro-group. A similar case, in which, however, this anomalous displacement is *not quantitative*, has recently been described by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339), who showed that 2:3:6-trinitrotoluene gave with alcoholic ammonia a mixture of 2:6-dinitro-*m*-toluidine and 3:6-dinitro-*o*-toluidine, the production of the latter base being another instance of the displacement of a nitro-group when contiguous to a methyl radicle (compare Kenner, T., 1914, **105**, 2717).

The orientation of the amino-group in 6-chloro-3-nitro-*o*-toluidine is demonstrated by the reactions summarised in the following diagram:



(XVIII.)

6-*Chloro*-2:3-*tolylenediamine* (XV), produced by reducing 6-chloro-3-nitro-*o*-toluidine with zinc dust and ammonium chloride in dilute alcohol, was obtained in the form of its hydrochloride (nacreous leaflets decomposing at 263°). The free base crystallised from benzene and light petroleum in colourless needles melting at 46—47°, and giving an *acetyl* derivative melting at

201—203°. The *diazoimine* (XVI), precipitated by adding sodium nitrite to the dihydrochloride in dilute acetic acid, crystallised from hot chloroform or benzene in creamy-white, flocculent masses of minute plates melting at 232° (Found: N=25·52; Cl=21·30. $C_7H_6N_3Cl$ requires N=25·08; Cl=21·16 per cent.).

2-Chloro-1-methylbenzophenanthrazine (XVIII), prepared by heating 6-chloro-2:3-tolylenediamine and phenanthraquinone in glacial acetic acid, crystallised from benzene in woolly masses of yellowish-white needles melting at 244° (Found: Cl=10·75. $C_{21}H_{13}N_2Cl$ requires Cl=10·79 per cent.).

Action of Ammonia on 2-Chloro-4:5-dinitrotoluene.

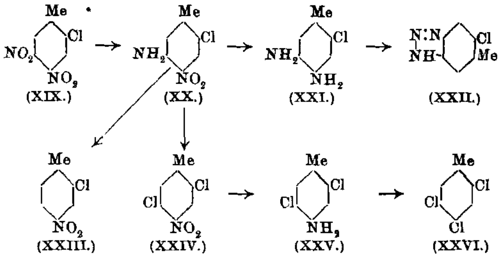
With liquid ammonia, the 4:5-dinitro-compound underwent far-reaching changes; ammonium nitrite and chloride were both produced, and the organic product was tarry and uncrystallisable. A simpler reaction occurred with saturated alcoholic ammonia, when 9 grams of the dinitro-compound yielded 8 grams of *6-chloro-4-nitro-m-toluidine* (XX), a base crystallising from methyl alcohol in stout, brittle, orange-red prisms with pyramidal ends, or in orange-red, silky needles: both forms melted at 144°.* This amine is slightly volatile in steam, even in the presence of mineral acid; it has a faint odour of vanilla, and is readily soluble in organic solvents, although sparingly so in water (Found: Cl=19·18; N=15·23. $C_7H_7O_2N_2Cl$ requires Cl=19·01; N=15·02 per cent.).

The processes summarised in the diagram on p. 790 were carried out in order to determine the constitution of 2-chloro-4:5-dinitrotoluene and 6-chloro-4-nitro-*m*-toluidine.

(1) On boiling an alcoholic solution of 2-chloro-4-nitrotoluene-5-diazonium sulphate, 2-chloro-4-nitrotoluene (XXIII) (m. p. 65°) was obtained, volatile in steam and developing an intense red coloration with hot alcoholic sodium hydroxide.

(2) The diazonium chloride when treated by the Sandmeyer reaction yielded 2:5-dichloro-4-nitrotoluene (XXIV) (m. p. 47—50°), and this product on reduction gave 2:5-dichloro-*p*-toluidine (XXV), melting at 91—92° (Cohen, T., 1901, **79**, 1130; 1902, **81**, 1347). A repetition of the Sandmeyer reaction on this base furnished 2:4:5-trichlorotoluene (XXVI), melting at 82°.

* A nitroamine stated to have the same orientation as the foregoing preparation, which has been described as separating in yellowish-brown prisms melting at 158—159°, was prepared by nitrating 6-chloroaceto-*m*-toluidide and by subsequent hydrolysis. A by-product obtained simultaneously was described as 6-chloro-2-nitro-*m*-toluidine (Badische Anilin- & Soda-Fabrik, D.R.-P. 226772).



(3) A similar diazo-solution, treated with excess of aqueous sodium carbonate and then added to an alkaline solution of resorcinol, gave a bright red azo-resorcinol, dyeing wood in orange-red shades not affected by after-chroming, which had evidently not lost the nitro-group.

6-Chloro-3:4-tolylenediamine (XXI).—The hydrochloride of this diamine was produced quantitatively by reducing 6-chloro-4-nitro-*m*-toluidine with zinc dust, ammonium chloride, and dilute alcohol, or with alcoholic stannous chloride. The free base crystallised in lustrous, pale brownish-yellow leaflets melting at 143° (Found: Cl = 22·35; N = 17·90. $C_7H_9N_2Cl$ requires Cl = 22·64; N = 17·89 per cent.).

The *diazoimine* (XXII), insoluble in water, crystallised from chloroform in pale flesh-coloured, woolly masses of minute needles melting at 192° (Found: Cl = 21·37; N = 25·33. $C_7H_6N_3Cl$ requires Cl = 21·16; N = 25·08 per cent.).

3-Chloro-2-methylbenzophenanthrazine, $C_{14}H_8{<}^{N}_{N}{>}C_6H_2MeCl$, obtained by heating its generators in glacial acetic acid, separated from benzene in golden-yellow needles melting at 264—265°. Like its isomeride (p. 789), it developed an intense cerise coloration with concentrated sulphuric acid (Found: Cl = 10·86. $C_{21}H_{13}N_2Cl$ requires Cl = 10·79 per cent.).

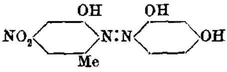
The Action of Ammonia on 2-Chloro-3:5-dinitrotoluene.

Dry ammonia gas passed to saturation into an alcoholic solution of 2-chloro-3:5-dinitrotoluene developed transient blue colorations, and then deposited 3:5-dinitro-*o*-toluidine (m. p. 213°), the yield being upwards of 95 per cent. Favourable results were obtained with methyl-alcoholic ammonia or with liquid ammonia. A similar

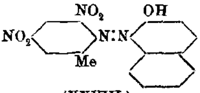
colour change was due to the formation of an additive compound with ammonia, since, on evaporating the violet solution in liquid ammonia, the residue consisted of unchanged 3:5-dinitro-compound, and was quite free from ammonium chloride or nitrite.

Azo-dyes from 3:5-*Dinitro-o-toluidine.*

3:5-Dinitro-*o*-toluidine* was diazotised either in concentrated sulphuric acid with solid sodium nitrite or by Witt's method, by adding a mixture in molecular proportions of the base and potassium metabisulphite to fuming nitric acid at -5° to 0°. The diluted diazo-solutions were neutralised by pouring into 3 per cent. aqueous sodium carbonate at 0°. A yellow, amorphous substance was deposited, the yield being about 30 per cent. of the base taken. The bright yellow filtrate, which contained a very stable diazo-compound, was added to an alkaline solution of resorcinol; the liquid was then heated on the water-bath, and sodium chloride was added to precipitate the alkali salt of the *azo*-dye. The free hydroxyazo-derivative (XXVII) separated from ether in lustrous,



(XXVII)



(XXVIII.)

crimson crystals decomposing at 256—257° (Found: N=14·10. $C_{13}H_{11}O_6N_3$ requires N=14·53 per cent.).

The *triacetyl* derivative of this hydroxyazo-dye, obtained by adding a trace of concentrated sulphuric acid to a suspension of the dye in acetic anhydride, crystallised from dilute acetic acid or alcohol in pale red needles melting at 147—148° (Found: N=10·38. $C_{19}H_{17}O_8N_3$ requires N=10·12 per cent.).

Further confirmation of the formula (XXVII) ascribed to the azo-resorcinol derivative was obtained by the fact that it dyed wool from an acid bath in orange-red shades, which were changed to dark purple tints by conversion into the chrome lake of the dye either by after-chroming or by the metachrome process.

3:5-*Dinitrotoluene*-2-*azo*-β-*naphthol* (XXVIII), produced by adding the dilute acid solution of 3:5-dinitrotoluene-2-diazonium sulphate to alkaline β-naphthol, crystallised from glacial acetic acid in lustrous, dark crimson needles melting at 226° (Found: N=16·53. $C_{17}H_{12}O_5N_4$ requires N=15·90 per cent.).

* This dinitro-base and the amines XII and XX (pp. 787 and 789) gave the Green and Rowe test for *o*- and *p*-nitroamines (T., 1913, 103, 508).

Colour Reactions of the 2-Chlorodinitrotoluenes.

The following colour changes were found useful in identifying the four isomeric 2-chlorodinitrotolnenes:

	Isomeride.	*Anhydrous* liquid ammonia (the gas liquefied on to the solid).	*Alcoholic* ammonia (gas passed into alcoholic solution).	Alcoholic sodium hydroxide.
1.	3 : 5- (m. p. 64·5°).	Intense violet to bluish-violet (red by transmitted light), changing to greenish-*black*.	Greenish to azure-blue, changing to red (tr.).	Pale yellow (tr.) to greenish-blue, to intense rose-red. On heating to bright orange-red (*tr.*).
2.	5 : 6- (m. p. 106·5°).	*Yellow* (*tr.*) *to* orange-red (tr.)	*Yellow* (*tr.*).	*Faint yellow* (*tr.*). On heating to orange, to deep orange-red, fading to brownish-yellow (tr.), finally light orange (tr.).
3.	4 : 5- (m. p. 88·5°).	Orange-red (tr.) to bluish- and brownish-black.	Orange-red (tr.).	Pale yellow (tr.) to intense emerald-green, to blue, bluish-black to brownish-red. On heating to pale orange-red (tr.).
4.	4 : 6- (m. p. 49°).	Intense violet to bluish-violet, to magenta and finally deep crimson.	Bright red (tr.) to *bluish-green*, to intense azure-*blue* (red by transmitted *light*), to deep crimson.	Intense blue to *greenish-blue*, *to* brownish-black, On heating to reddish-black, and finally to deep orange-red (tr.).

In all cases, the colorations were opaque unless marked "tr." = transparent. Intense violet and blue colorations with anhydrous and alcoholic ammonia were obtained with both meta-dinitro-compounds, whereas the two ortho-dinitro-isomerides gave orange-red tints.

Summary.

(1) The nitration of *o*-chlorotoluene in mixed nitric–sulphuric acid leads to a mixture of isomeric dinitro-compounds (90 per cent. of the calculated amount). The loss is occasioned by oxida-

tion and sulphonation. The nitration mixture contains four isomerides in approximately the following percentage amounts:

	Per cent.
3 : 5-Dinitro-2-chlorotoluene	55—60
5 : 6- „ „	18—20
4 : 5- „ „	18—20
4 : 6- „ „	1— 2

(2) The existence of the four isomeric dinitro-2-chlorotoluenes in the nitration mixture shows that the orientation due to methyl is not entirely overpowered by that of the more actively directive chlorine substituent. The influence of the methyl group is more powerful in the first stage of nitration, when it accounts for 38 per cent. of the mono-nitrated products (Wibaut, *loc. cit.*), whereas in the second stage of the process its effect accounts for less than 10 per cent. of the final product.

(3) Nitration of 2-chloro-6-nitrotoluene leads to the formation of 2-chloro-5 : 6-dinitrotoluene as main product, the yield of this isomeride being about 90 per cent.

(4) Nitration of 2-chloro-4-nitrotoluene gives 2-chloro-4 : 5-dinitrotoluene as main product (upwards of 85 per cent.) and 2-chloro-4 : 6-dinitrotoluene as by-product (yield about 12 per cent.).

(5) These dinitro-2-chlorotoluenes contain labile acid radicles displaceable by amino-groups. In this reaction, addition of ammonia to the aromatic compound precedes substitution, the first phase in the reaction being accompanied by the development of intense colorations.

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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LXXXVI.—*The Oxidation of the Ingredients of Banded Bituminous Coal. Studies in the Composition of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

IT has been shown that the four macroscopically distinct portions, vitrain, clarain, durain, and fusain, into which banded bituminous coal can be separated differ in essential microscopical structure (Stopes, *Proc. Roy. Soc.*, 1919, [*B*], **90**, 470), in their behaviour towards reagents and on destructive distillation (Tideswell and Wheeler, T., 1919, **115**, 619), in their behaviour on coking, and in the composition of their mineral constituents (Lessing, this vol., pp. 247, 256). The differences in chemical constitution between the ingredients disclosed by a decrease in their reactivity towards solvents, reagents, and heat-treatment (in the order vitrain, clarain, durain), seem to be due to a variation in the proportions in which the constituents of the coal conglomerate are present in each ingredient of the banded coal rather than to the presence in any one of them of fundamentally distinct types of compounds. Fusain, which is much less reactive in most respects than the remainder of the coal substance, requires separate consideration.

In view of their known differences, the separate ingredients of banded coal are more suitable materials for the study of the oxidation of "coal" in relation to its spontaneous combustion than are bulk samples. For it is clear that lumps of banded coal, although obtained by careful quartering of the bulk samples, may differ markedly one from another, in chemical composition and general properties, dependent on the distribution of the different bands in them.

Samples of the four ingredients from the Hamstead Thick Coal have been subjected to the action of air or oxygen at different temperatures to determine their rates of oxidation and relative ignition-temperatures. The experiments were designed to yield, in addition to information as to the comparative behaviour of the four ingredients of banded coal, data which would be of service to the general research on the mechanism of the reaction between oxygen and the coal conglomerate on which we are engaged.

Relative Ignition-temperatures.

The method of experiment has been described in T., 1918, **113**, 949, which should be consulted. Insufficient fusain was available for the determination: the other ingredients did not show any marked differences in their relative ignition-temperatures as judged by the points of intersection of the time–temperature curves. The tests were carried out under identical conditions as regards rate of heating, speed of passage of air-current, etc., and the "ignition-temperatures" recorded ranged from 170° to 175° for each ingredient.

It was clear, however, from the difference in slope of the heating-curves for the coals compared with that for the sand-bath, that the wide differences in the amounts of moisture contained in the three ingredients affected in a different degree in each instance the rate of rise of temperature of the coal due to oxidation. The moisture-content chiefly determines the lag at low temperatures (up to 80°) between the temperature of the coal and that of the sand-bath, and this lag affects the point of intersection of the two curves. Consideration of the rates of heating of the coals at temperatures above 80° (at which temperature nearly all moisture had been driven off) indicated that vitrain and clarain were almost equally liable to self-heat, whilst durain appeared appreciably less liable.

Rate of Absorption of Oxygen.

The apparatus employed, constructed wholly of glass without rubber connexions, enabled a continuous stream of air or oxygen to be circulated through the sample of coal to be tested, which was contained in a horizontal reaction-tube, 1·5 cm. in diameter, maintained at the experimental temperature by means of an electrically heated air-oven. Suitable stop-cocks in the circuit enabled the reaction-tube to be by-passed, or to be exhausted separately from the rest of the apparatus. A by-passed calcium chloride tube, for drying the gases, was included in the circuit.

Twenty grams of the coal, undried and broken into pieces capable of passing through a 10 × 10 and remaining on a 60 × 60 mesh sieve, were packed tightly in the reaction-tube and held in position by plugs of glass-wool. The coal was then exhausted during forty-eight hours at the ordinary temperature, and finally at 200°, the gases removed (original occluded gases) being collected and analysed. In the meantime, the remainder of the apparatus (the volume of which could be adjusted to be 1100, 2100, or

3100 c.c. as required) had been filled with oxygen at rather more than atmospheric pressure, and circulation begun, through the by-pass of the reaction-tube, by means of an automatic mercury pump.

The coal having been brought to the experimental temperature, the reaction-tube was included in the circuit, which formed a closed system, and readings of the gas pressure were at once taken. Thereafter, readings of the temperature, gas pressure, and barometer were taken at frequent intervals during 120 hours, the rate of circulation of the oxygen through the coal being maintained at 1 litre per hour.

At the end of the circulation period of each experiment (which yielded time-pressure curves, from which the rate of absorption of oxygen by the coal could be calculated), the coal was rapidly cooled to the ordinary temperature, and the gases remaining in the reaction tube were removed by exhaustion during several hours and transferred to the main part of the apparatus. The temperature of the coal was then raised to 200°, and the gases obtained by exhaustion during twenty-four hours were collected separately and analysed. A sample of the oxygen (containing carbon dioxide and carbon monoxide) in the main part of the apparatus was also taken. After allowing the reaction-tube to cool to the temperature required for the next experiment, fresh oxygen was introduced into the apparatus, and the cycle of operations repeated. In the series of oxidations of vitrain, clarain, and durain, the temperatures were 15°, 50°, 100°, 50°, and 50°; with fusain the order was 50°, 50°, 15°, 100°, and 50°.

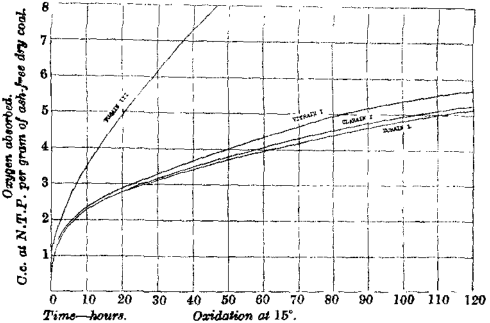
In Figs. 1, 2, and 3, curves are given showing the relation between time and the volume of oxygen absorbed by each of the ingredients of the banded Hamstead coal at 15°, 50°, and 100°. The series of oxidations at the three temperatures were made with each ingredient on the same sample, which was not removed from the absorption apparatus until the series relating to it was completed. Before each oxidation at a given temperature, the coal, in position in the absorption apparatus, was exhausted at 200°, as already described, until gases ceased to be evolved.

It has been shown (T., 1918, **113**, 949; 1919, **115**, 895) that, in a manner analogous to the burning of carbon, the immediate result of the absorption of oxygen by coal may be considered to be the formation of a coal-oxygen complex. This complex on being raised slightly in temperature decomposes, evolving carbon dioxide, carbon monoxide, and water, and leaving a residue but little altered in character from the original coal.

Preliminary experiments had shown that it was possible to heat

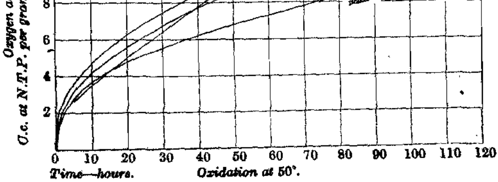
the Hamstead coal "saturated" with oxygen to a temperature as high as 200°, and to exhaust it at that temperature, without

FIG. 1.



materially altering the composition of the coal substance or producing any effects other than to decompose the coal–oxygen complex

FIG. 2.

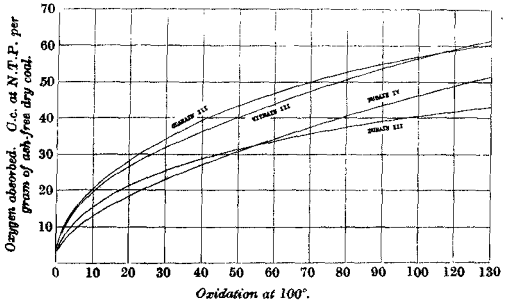


and to remove small quantities of gaseous paraffin hydrocarbons (the higher members of the series). The proportion of the complex

that decomposes into the simple oxides increases rapidly with increased temperature; hence the necessity for exhausting the "saturated" coal at as high a temperature as possible. By such exhaustion, the coal recovers to a great extent its capacity for absorbing oxygen—that is to say, its capacity for complex-formation—the recovery amounting to about 95 per cent. of the original capacity after exhaustion at 200°. It may be noted that the Hamstead coal is particularly adapted to experiments of this nature by reason of the small quantities of occluded paraffins that it contains.

A study of the absorption curves discloses differences between the three ingredients, vitrain, clarain, and durain, of the same order

Fig. 3.



as might be anticipated from their differences in composition. All three absorb oxygen to a marked degree, but there is a decrease in absorptive power in the order vitrain, clarain, durain which is particularly marked at low temperatures (15°). At higher temperatures (50°), the difference between vitrain and clarain decreases, and at 100° the absorptive power of each is nearly the same. It is possible that at still higher temperatures clarain would take the lead. Durain, throughout the series of experiments, displayed less absorptive power than either vitrain or clarain, the absorption of oxygen by durain being 10 per cent. less than by vitrain at 15° and 30 per cent. less at 100°.

The temperature-coefficients of the reactions (K_{10}), calculated from the total absorptions during 120 hours, are:

Temperature range :	Vitrain.	Clarain.	Durain.	Fusain.
15—50°	1·301	1·298	1·217	1·538
50—100°	1·407	1·414	1·387	1·013
Mean value over :				
15—100°	1·362	1·365	1·313	1·203

Fusain stands apart from the rest of the coal, as in its chemical properties generally, in its high absorptive power at low temperatures, and its low temperature-coefficient. At 100°, fusain absorbs oxygen scarcely more readily than does durain.

The ease of oxidation of the four ingredients of Hamstead coal should be compared with their power of absorbing moisture and the halogens:

	Vitrain.	Clarain.	Durain.	Fusain.
Moisture-content, per cent.	12·40	11·95	7·00	4·30
Absorption of iodine, per cent.				
(*a*) Aqueous, in 24 hours	33·5	34·0	26·6	6·4
(*b*) Wijs' *solution, in* 6 hours	86·5	84·0	68·4	12·8
Absorption of oxygen, c.c. per gram.				
At 100° in 120 hours	60·9	60·3	43·2	51·6

Whilst the absorption of oxygen and the halogens by coal is certainly not entirely a physical phenomenon, the magnitude of the effect for a coal of given composition may well be proportional to the concentration of the oxygen or the halogens maintained within it by purely physical absorption. In this connexion, the observation by Winmill (*Trans. Inst. Min. Eng.*, 1916, **51**, 494) may be cited, that the rate of absorption of oxygen by coal varies approximately as the square root of the partial pressure of the oxygen. Such a relationship would be expected were the amount of oxygen entering into chemical combination in a given time with the coal substance dependent on the concentration of oxygen within the coal.

Judged from this point of view, the difference in absorptive power evinced by the three ingredients, vitrain, clarain, and durain, would lie in their physical structure—in their power of physical absorption. This does not necessarily imply that the subsequent chemical action, or the products of such action, are identical in each instance, although there is undoubtedly a great similarity between them.

The data obtained by the exhaustion of the oxidised coals at 200° throws some light on this matter. The main facts elicited from a study of the quantities and compositions of the gases thus obtained (see tables I and II) are:

(1) There is a rapid and continuous increase in the amount of gas evolved (that is to say, in the amount of decomposition of the coal-oxygen complex) as the temperature of exhaustion of the coal after oxidation is increased.

TABLE I.

Gases Evolved on Exhaustion.

Temperature during exhaustion.	*A.* From durain, after oxidation at 100°. C.c. CO_2.	*A.* CO.	*B.* From same sample of durain (after experiment *A*), after oxidation at 50°. C.c. CO_2.	*B.* CO.
15—100°	2·7	0·7	3·1	0·8
100—150°	18·5	5·2	4·5	1·6
150—200	63·8	15·1	15·8	4·5

TABLE II.

	Series Number.	Temperature of oxidation.	Vitrain.	Clarain.	Durain.	Fusain.
Oxygen absorbed. C.c. per gram of ash-free dry coal.	I.	15°	5·7	5·2	5·15	12·63
	II.	50	13·4	12·5	9·9	45·0
	III.	100	60·9	60·3	43·2	51·6
	IV.	50	9·2	9·5	7·0	15·0
	V.	50	8·8	8·3	5·9	10·0
Carbon dioxide evolved on exhaustion at 200°.	Original occluded gases.		1·61	1·30	0·90	1·06
	I.	15	0·59	0·60	0·49	0·32
	II.	50	1·71	1·38	1·13	0·77
	III.	100	6·85	6·40	4·79	4·55
	IV.	50	3·28	2·20	1·91	—
	V.	50	2·68	1·60	1·80	1·29
Carbon monoxide evolved on exhaustion at 200°.	Original occluded gases.		0·30	0·26	0·16	0·25
	I.	15	0·16	0·17	0·13	0·10
	II.	50	0·48	0·40	0·30	0·27
	III.	100	1·65	1·60	1·19	1·29
	IV.	50	0·72	0·67	0·51	—
	V.	50	0·58	0·47	0·45	0·38
Ratio CO_2/CO evolved on exhaustion at 200°.	Original occluded gases.		5·35	5·08	5·50	4·10
	I.	15	3·64	3·60	3·73	3·10
	II.	50	3·54	3·44	3·74	2·95
	III.	100	4·57	3·99	4·00	3·52
	IV.	50	4·54	3·40	3·73	—
	V.	50	4·62	3·40	4·06	3·40

(2) The amount of complex formed, as judged by the volumes of carbon dioxide and carbon monoxide subsequently evolved on exhaustion at 200°, increases rapidly with the temperature of oxidation.

(3) There is a variation in the amount of decomposition of the complex dependent on the previous treatment to which the coal has been subjected. This was most marked after the coal had been

oxidised at 100° and exhausted at 200°. Before this treatment, oxidation at 50° (Series No. II) and exhaustion at 200° released as carbon dioxide and carbon monoxide 12 per cent. of the oxygen absorbed at 50°; subsequently (Series Nos. IV and V), 40 per cent. was so released.

(4) There is a difference between the four ingredients as regards the ease of decomposition of the complex, the proportion of the absorbed oxygen released as carbon dioxide and carbon monoxide being considerably less with clarain than with vitrain or durain (except after oxidation at 15°). This suggests that the chemical reaction which follows the physical absorption of oxygen, and is responsible for its final disappearance, varies somewhat in degree, and perhaps also in nature, as between one ingredient of the banded coal and another. With fusain, the oxygen complex is either formed to a less extent than with the other parts of the coal, or, when formed, is more difficult to decompose.

The general conclusions to be drawn from the experiments as regards the banded bituminous coal are:

(1) Of the three main ingredients of the banded coal, the bright ones, vitrain and clarain, show greater liability to oxidise and to ignite than the dull durain. The difference between these ingredients is not, however, so great as to warrant any suggestion that the bright portions of Hamstead coal are primarily responsible for its liability to spontaneous combustion.

(2) The influence of fusain is uncertain. Many practical miners consider that spontaneous combustion originates where "mother-of-coal" (fusain) abounds. The results of our experiments lead us to consider it improbable that fusain has a preponderating influence in determining the actual ignition of the coal after self-heating has begun; but it is conceivable that the rapid absorption of oxygen by fusain at low temperatures may be attended by a sufficient evolution of heat to raise appreciably the temperature of the main mass of the coal, thereby causing the most inflammable ingredient (vitrain) to react more readily with oxygen.

To determine this matter with certainty, and it is clearly one which demands settlement, further experiments with a number of samples of fusain from different coals are required. We are addressing ourselves to this problem as being part of the general study of the oxidation of coal.

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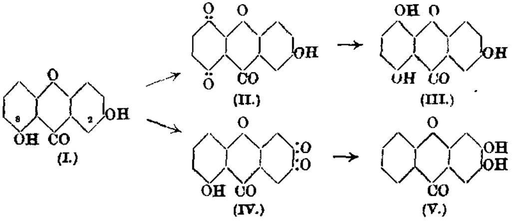
LXXXVII.—8-*Hydroxy*-2 : 3-*quinoxanthone*.

By Harry Fitzgibbon Dean and Maximilian Nierenstein.

When euxanthone (I) is oxidised with chromic acid, a red product is formed, to which the formula 2-hydroxy-5 : 8-quinoxanthone (II) has been assigned (Nierenstein, *Ber.*, 1913, **46**, 649). On reduction, this substance yields the corresponding pale yellow 2 : 5 : 8-trihydroxyxanthone (III). Van Scherpenberg (*Diss.*, Delft, 1918, 68; *Chem. Weekblad*, 1919, **16**, 1146) has pointed out that since the quinoxanthone gives trinitroresorcinol on treatment with nitric acid, its probable constitution is 8-hydroxy-2 : 3-quinoxanthone (IV), the reduction product being the corresponding 2 : 3 : 8-trihydroxyxanthone (V). These contentions of van Scherpenberg are in the best agreement with the results given in the present communication.



Experimental.

The original method for the oxidation of euxanthone was found, as previously stated (*loc. cit.*), to give a product which crystallised only with difficulty. This may be overcome by using the following modification: To a well-cooled solution of 5 grams of euxanthone in 75 c.c. of glacial acetic acid, 10 grams of chromic acid dissolved in 150 c.c. of glacial acetic acid, also well cooled, are slowly added during three hours. The mixture is kept on ice for twenty-four hours, water is then added, and the precipitate crystallised from glacial acetic acid. This product gives all the colour reactions previously described. The average yield is 70 per

cent. of the theoretical (Found: C=64·5; H=2·7. Calc.: C=64·5; H=2·5 per cent.). Preparations which may be readily crystallised are also obtained when 2:3:8-trihydroxyxanthone (V) is oxidised with *p*-benzoquinone (A. G. Perkin, T., 1913, **103**, 657). A solution of 1 gram of the trihydroxyxanthone in 25 c.c. of absolute alcohol is treated in the cold with 0·5 gram of *p*-benzoquinone, and the solid formed is crystallised from glacial acetic acid. The average yield is 73 per cent. of the theoretical (Found: C=64·3; H=2·6. Calc.: C=64·5; H=2·5 per cent.).

On heating molecular proportions of the quinoxanthone (prepared by the original or by either of the above-given methods) with 3:4-tolylenediamine in glacial acetic acid solution, the corresponding *azine* is easily obtained, which conclusively proves the ortho-quinonoidal structure of the compound. The azine crystallises from glacial acetic acid in deep red needles, which darken and subsequently char between 328° and 340° without melting (Found: N=8·3, 8·7. $C_{20}H_{14}O_3N_2$ requires N=8·5 per cent.).

2:3-*Methylenedioxy-8-methoxyxanthone.*

As in the case of *iso*quercetone (Nierenstein, T., 1915, **107**, 870), an excess of diazomethane converts the quinone into the above-mentioned derivative. The reaction is carried out in ethereal suspension, the theoretical yield being obtained. The substance crystallises from alcohol in colourless needles, which melt and decompose at 211—212° (Found: C=66·5; H=3·8; OMe=11·0. $C_{15}H_{10}O_5$ requires C=66·7; H=3·7; OMe=11·5 per cent.).

2:3-*Dihydroxy-8-methoxyxanthone.*

This substance is obtained on removing the methylene group by Fittig and Remsen's method (*Annalen*, 1873, **168**, 97), the technique being the same as in the case of the corresponding *iso*quercetone derivative (*loc. cit.*). It crystallises from alcohol in colourless needles, which melt and decompose at 249—251°. The alcoholic solution gives a green colour with alcoholic ferric chloride. It dyes calico mordanted with aluminium faintly, thus resembling 2:3-dihydroxyxanthone (Liebermann and Lindenbaum, *Ber.*, 1904, **37**, 2736) (Found: C=64·8; H=4·2. $C_{14}H_{10}O_5$ requires C=65·1; H=3·9 per cent.).

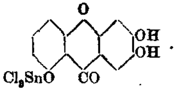
2:3:8-*Trimethoxyxanthone.*

This derivative is prepared from the previously-mentioned dihydroxy-compound by the action of methyl sulphate. It

crystallises from alcohol in faintly yellow needles, which melt at 194—195°. This substance is identical with that formerly described as 2:5:8-trimethoxyxanthone, which was prepared by the action of diazomethane on the corresponding trihydroxy-xanthone.

2:3-*Diacetoxy*-8-*methoxyxanthone*, prepared by digesting the dihydroxy-compound with acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in colourless needles, which melt and decompose at 231—232° (Found: C=63·0; H=4·3. $C_{18}H_{14}O_7$ requires C=63·2; H=4·1 per cent.).

The relative positions of the hydroxyl groups in 2:3:8-tri-hydroxyxanthone (V) become still more evident on comparison with euxanthone (I). (1) 2:3:8-Trihydroxyxanthone, on treatment with methyl sulphate (3½ mols.), is not fully methylated, the hydroxyl group in position 8 not being attacked, as in the case of euxanthone (v. Kostanecki, *Ber.*, 1894, **27**, 1992; Herzig and Klimosch, *ibid.*, 1908, **41**, 3894; compare, however, A. G. Perkin, T., 1913, **103**, 1632, who finds that under certain conditions alkylation of this type of hydroxyl group may take place). (2) The resulting 8-hydroxy-2:3-dimethoxyxanthone is coloured, forms yellow solutions with alkalis, and possesses tinctorial properties similar to 8-hydroxy-2-methoxyxanthone (Herzig and Klimosch, *loc. cit.*; compare also Perkin and Everest, "The Natural Organic Colouring Matters," p. 125). (3) Like euxanthone (Pfeiffer, *Ber.*, 1911, **44**, 2653; compare also Herzig and Schönbach, *Monatsh.*, 1912, **33**, 673), 2:3:8-trihydroxyxanthone reacts with stannic chloride, forming the compound,



The corresponding tin compound is also obtained from 8-hydroxy-2:3-dimethoxyxanthone. 2:3-Dihydroxy-8-methoxyxanthone gives quite unexpectedly the same substitution product as 2:3:8-trihydroxyxanthone.

2:3:8-*Trihydroxyxanthone differs, however, in one way from* euxanthone. It has been shown (Herzig, *Monatsh.*, 1891, **12**, 161; 1897, **18**, 700; Herzig and Klimosch, *ibid.*, 1909, **30**, 527) that when euxanthone is methylated with diazomethane, 2-hydroxy-8-methoxyxanthone is formed, the 2-hydroxy-group not being susceptible to any form of methylation. This is not the case when 2:3:8-trihydroxyxanthone is methylated with diazomethane, all

three hydroxy-groups behaving in a similar manner, as previously shown (*loc. cit.*). Also 2:3-dihydroxy-8-methoxyxanthone, when methylated with methyl sulphate, yields the trimethoxy-derivative, as described above.

8-*Hydroxy*-2:3-*dimethoxyxanthone*, prepared by the action of methyl sulphate ($3\frac{1}{2}$ mols.) on an alcoholic solution of the trihydroxyxanthone, crystallises from alcohol in faintly yellow needles, which melt and decompose at 228—231°. It dissolves in dilute sodium hydroxide with a yellow colour, and dyes calico mordanted with aluminium faintly. Diazomethane converts it quantitatively into the corresponding trimethoxyxanthone (m. p. 195°) (Found: C=66·0; H=4·7; OMe=22·8. $C_{15}H_{12}O_5$ requires C=66·2; H=4·4; OMe=22·8 per cent.).

8-*Acetoxy*-2 : 3-*dimethoxyxanthone*, prepared in the usual manner, crystallises from alcohol in colourless needles, which melt and decompose at 224—225° (Found: C=65·2; H=4·7. $C_{17}H_{14}O_6$ requires C=65·0; H=4·4 per cent.).

Action of Stannic Chloride on 2:3:8-*Trihydroxyxanthone.*

One gram of the trihydroxyxanthone dissolved in 75 c.c. of *s*-tetrachloroethane was heated with 2 grams of stannic chloride dissolved in 50 c.c. of the same solvent. The solution was kept at the boiling point for two hours, and the solid collected and washed, at first with *s*-tetrachloroethane and subsequently with benzene. Great care was taken to avoid the presence of moisture. The product was crystallised from *s*-tetrachloroethane, from which it separated in deep red crystals. These did not melt below 330°, but darkened at about 285—290°. When dissolved in boiling pyridine, a red solution with a blue fluorescence is obtained. The compound is slowly decomposed by water at the ordinary temperature; boiling greatly accelerates the decomposition. The analysis of this substance and of the other tin compounds was carried out according to the methods given by Pfeiffer (*Annalen*, 1910, **376**, 344) (Found: Cl = 22·2; Sn = 25·5. $C_{13}H_7O_5Cl_3Sn$ requires Cl=22·7; Sn=25·4 per cent.).

Action of Stannic Chloride on 8-*Hydroxy*-2:3-*dimethoxyxanthone.*

Five grams of the substance dissolved in benzene were heated with 4 grams of stannic chloride in 50 c.c. of benzene for two hours. The product was collected, washed with dry benzene, and thoroughly dried in a vacuum over phosphoric oxide. The substance dissolves in pyridine with a pale orange colour; it is insoluble in alcohol or benzene. Water decomposes it on keeping

and on boiling. The substance has no definite melting point, *decomposing* at about 311—325°. The *yield* was 7·8 *grams* (Found: Cl = 21·6, 21·2; Sn = 24·8, 24·6. $C_{15}H_{11}O_5Cl_3Sn$ requires Cl = 21·4; Sn = 24·0 per cent.).

Action of Stannic Chloride on 2:3-Dihydroxy-8-methoxyxanthone.

When 1 gram of the monomethoxy-derivative dissolved in 50 c.c. of *s*-tetrachloroethane is heated with 1 gram of stannic chloride in 50 c.c. of the same solvent, no precipitate is at first formed. After three-quarters of an hour's heating, the substitution product commences to appear, the reaction being completed in six hours. So far as it is possible to judge, the product is identical with that formed when 2:3:8-trihydroxyxanthone reacts with stannic chloride. For the analyses, two different preparations were used (Found: Cl = 22·6, 22·9; Sn = 25·9, 25·7. Calc.: Cl = 22·7; Sn = 25·4 per cent.).

In view of these results, the compound previously described (*loc. cit.*) as 2:5:8-triacetoxyxanthone is now considered to be 2:3:8-triacetoxyxanthone.

We are indebted to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

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[*Received, June 1st, 1920.*]

LXXXVIII.—*The Decomposition of Nitric Esters.*

By Robert Crosbie Farmer.

In a recent paper on the decomposition of nitric esters by lime (this vol., p. 552), Lowry, Browning, and Farmery have expressed the view that the primary decomposition of nitric esters is not a hydrolysis, but a decomposition to aldehyde (Berthelot), possibly through an alcohol peroxide (Klason and Carlson). Their grounds for this belief are the almost complete absence of glycerol in the products of decomposition of glyceryl trinitrate (and of the corresponding alcohols in other cases) and the fact that this formulation would give, as the primary decomposition product of glyceryl trinitrate, the dialdehyde, CHO·CO·CHO, which would conveniently account for many of the products which are actually

found to result. This mechanism of the decomposition of glyceryl trinitrate was previously suggested by Berl and Delpy (*Ber.*, 1910, **43**, 1421), who regarded it, however, as a secondary reaction preceded by a hydrolysis. The latter view is so strongly supported by experimental evidence that Lowry, Browning, and Farmery's criticism of the views of Silberrad and Farmer (T., 1906, **89**, 1759) cannot be upheld.

From the nature of the hydroxy-acids, etc., isolated by Silberrad and Farmer (T., 1906, **89**, 1182) and others, the intermediate formation of the above aldehyde, although hypothetical, is readily conceivable. It does not, however, by any means follow that such aldehydes represent the initial stage of the decomposition. If we go back to first principles, it is clear that the nitric group has oxygen to spare, whilst the carbon nucleus is ready to take up oxygen. When hydrolytic agents are added (acid or alkali), the structure is loosened, in accordance with the general behaviour of esters; at the moment of splitting, however, the carbon nucleus is in a condition so sensitive to oxidation that the alcohol and acid are not actually formed, or are formed only to a minor extent. This was clearly brought out by Silberrad and Farmer, who showed that, if once formed as complete molecules, they do not interact at the dilutions in question (although, as is well known, glycerol can be oxidised to aldehydes and ketones by nitric acid under suitable conditions). The acid and alcohol groups must react, therefore, with the formation of oxidation products of the alcohol. This is tantamount to saying that the nitric acid in the moment of its formation oxidises the carbon nucleus. Beyond this, the rest of the process may well proceed as indicated by Lowry, Browning, and Farmery.

The primary hydrolysis is in accordance with the universal behaviour of esters, and it would require much more than speculative evidence to justify the view that nitric esters form an exception to the general rule. If some other form of primary decomposition did occur, it would at least appear inevitable that hydrolysis should take place concurrently, and thus we are driven in any case to the conclusion that the nitric acid in the moment of formation oxidises the alcohol nucleus whenever the alcohol is not found as a product of the reaction.

Regeneration of Alcohols from Nitric Esters.

The basis of the argument against hydrolysis is that the alcohol is not ordinarily found as a product of the decomposition. In view of this, it is somewhat surprising that Lowry, Browning, and Farmery claim to have shown that nitrocellulose breaks down in

successive stages to cellulose trinitrate and dinitrate, for this would clearly imply that a normal hydrolysis of a nitric ester group can take place. No weight can, however, be attached to this, as it is clear from numerous investigations that no such definite stages can be isolated in the cellulose nitrates, and the approximate agreement of the nitrogen percentage is purely accidental (compare, for example, Will, *Ber.*, 1891, **24**, 400). It has been shown by Berl and Fodor (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1910, 5, 254, 269) that the partial decomposition by alkalis is of a much more complex nature.

Ample evidence is, however, obtainable in the case of other esters that the nitric group can undergo normal hydrolysis. The following evidence is based partly on acid hydrolysis and partly on alkaline. There appears to be no reason to differentiate, in principle, between these. The same products are obtained in both cases, and as regards the velocity of hydrolysis, it is shown later in the present work that the relationship between acid and alkaline hydrolysis of nitrocellulose is so closely in accord with that of other esters that it can scarcely be supposed that the one is hydrolytic without accepting this for the other.

The data in the present paper refer mainly to the glyceryl nitrates. It is shown, in the first place, that glyceryl trinitrate is hydrolysed by dilute nitric acid under suitable conditions to glycerol, according to the equation

$$C_3H_5(NO_3)_3 + 3H_2O = C_3H_5(OH)_3 + 3HNO_3.$$

It is also shown that the hydrolysis of glyceryl dinitrate can take place with practically no reduction of the nitric acid and practically no formation of organic acids. It is already known that methyl nitrate is hydrolysed to dimethyl ether by alkali, no internal oxidation taking place. It would be difficult to reconcile this with the primary formation of an aldehyde.

In most cases, hydrolysis is accompanied by much internal oxidation, but this can be overcome in various ways. Thus the normal hydrolysis of the nitric group,

$$R\cdot NO_3 + H_2O = R\cdot OH + HNO_3,$$

becomes the main reaction whenever the conditions are such that either the oxidising action of the nitric acid is suppressed or the alcohol is rendered immune against oxidaton.

Suppression of the Oxidising Action of the Nitric Acid.

(*a*) *By Reducing Agents.*—In the presence of these, the nitric group cannot oxidise the alcohol, and in this case the alcohol is formed just as in a normal hydrolysis. This is well known in the

case of sulphides (Bloxam, *Chem. News*, 1883, **47**, 169), and was shown by Klason and Carlson (*Ber.*, 1906, **39**, 2752; 1907, **40**, 4183, 4191) to hold also for alkaline hydrolysis in the presence of phenyl mercaptan or hydrogen peroxide. Gutmann (*Ber.*, 1908, **41**, 2052) showed that sodium arsenite acted similarly. Brühl had previously formulated nitric acid and its esters as derivatives of hydrogen peroxide on the basis of spectrometric measurements (*Ber.*, 1898, **31**, 1350), and Klason and Carlson assumed that these esters were hydrolysed to hypothetical alcohol peroxides, which were then reduced to the alcohols. This is a totally unnecessary assumption; their work simply shows that when a reducing agent is present to remove the nascent nitric acid, the normal hydrolysis occurs. The action of hydrogen peroxide seems, indeed, rather incompatible with the assumption of a peroxide, as it is scarcely likely that hydrogen peroxide would react with a derivative of itself in the manner indicated. Cambi (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 301) has opposed the peroxide formula of nitric acid and its esters. He points out, for instance, that the quantitative oxidation of nitrous to nitric acid by permanganate is not in accordance with this formulation.

(*b*) *By Sulphuric Acid*.—In the presence of sulphuric acid of moderate strength, the oxidising action of nitric acid is decreased, as is commonly experienced in its action on toluene, etc. If, therefore, nitroglycerin is hydrolysed with 70 per cent. sulphuric acid, the nitric acid does not attack the organic residue to any great extent, and glyceryl dinitrate is formed in good yield D.R.-P. 175751). Similarly, glyceryl dinitrate is hydrolysed by 0 per cent. sulphuric acid to glyceryl mononitrate and glycerol Will, *Ber.*, 1908, **41**, 1107).

Protection of the Alcohol from Oxidation.

(*a*) *By Continuous Abstraction as Glycerophosphoric Acid*.—It shown in the present work that if glyceryl trinitrate is hydro'sed by phosphoric acid, the glycerol is converted to glycerohosphoric acid, and is thus protected from the oxidising action f the nitric acid. The intermediate formation of an alcohol eroxide or aldehyde appears in this case to be excluded.

(*b*) *By the Presence of further Nitric Groups*.—When the lcohol contains further nitric groups, it is less susceptible to xidation than in the absence of such groups. In accordance with ıis, one of the nitric groups of glyceryl trinitrate can be readily ydrolysed to the alcohol group. Thus, if we represent the group $(CH_2{\cdot}NO_3)_2CH{\cdot}$ by R, the decomposition takes the form of a ormal hydrolysis, $R{\cdot}NO_3 + H_2O = R{\cdot}OH + HNO_3$. This holds both

for acid and alkaline hydrolysis; thus it is shown in the present work that hydrolysis of glyceryl trinitrate by dilute nitric acid yields glyceryl dinitrate, and Berl and Delpy (*Ber.*, 1910, **43**, 1421) have found the same reaction to take place in the presence of alkalis. Lowry, Browning, and Farmery have conceded that such partial hydrolysis can occur, and it appears strange that with such distinct evidence of the normal hydrolysis of a nitric ester group they should still refuse to recognise this as the first stage in the decomposition.

It is seen, therefore, that whenever the alcohol is protected by any means from oxidation, it is readily obtained as a product of the decomposition. It would be difficult to explain these results in any other way than that the primary reaction is a hydrolysis. This aspect is in no way contrary to the experimental evidence of Lowry, Browning, and Farmery. On the other hand, it is in complete accord with the general nature of the decomposition of nitrocellulose, etc. The whole experience of the behaviour of these esters on storage and in climatic trials (see Silberrad and Farmer, *J. Soc. Chem. Ind.*, 1906, **25**, 961) leaves no doubt that the decomposition is hydrolytic in nature.

Not only is the hydrolysis brought about by the same agencies as in the case of other esters (hydrogen and hydroxyl ions), but the relative velocities are of the order that would be expected for ester hydrolysis. When alkali is added to nitrocellulose, a moderately rapid hydrolysis occurs. The velocity decreases as the alkali is neutralised. When the solution becomes neutral, the hydrolysis becomes very slow, but does not cease entirely, owing to the slight ionisation of the water. Thus the solution gradually becomes acid, and the velocity again increases, but is very much less for the hydrogen ions than for hydroxyl ions, namely, in the ratio of 1 to 480 (Silberrad and Farmer, T., 1906, **89**, 1759). The relative velocities of hydrolysis of esters by acids and alkalis vary somewhat considerably, but the general relationship may be seen from the aliphatic esters examined by de Hemptinne (*Zeitsch. physikal. Chem.*, 1892, **13**, 493). The following table shows the velocity constants at 25°:

	Alkali.	Acid.	Ratio.
Methyl acetate	9·66	0·00659	1466
Ethyl acetate	6·38	0·00682	935
Propyl acetate	5·31	0·00671	791
Ethyl propionate	5·61	0·00727	772
Ethyl butyrate	3·39	0·00417	813

Thus the ratio found for nitrocellulose appears quite reasonable, considering that the hydrolysis is abnormal in nature.

In the figure is shown the course of the hydrolysis of nitro-

cellulose in the neighbourhood of the minimum velocity, which is seen to occur slightly on the acid side of the neutral point. The course of the hydrolysis is so characteristic of that of esters that this forms a distinct confirmation of the view that hydrolysis is the primary reaction, both in the presence of acids and of alkalis.

A knowledge of the hydrolytic behaviour of nitric esters has a close bearing on the action of "stabilisers," which are added to explosives (compare Marshall, "Explosives," 1917, p. 640). The idea of adding alkalis to neutralise the acid formed was advocated as early as 1849 (Maurey, *Compt. rend.*, 1849, **28**, 343), and followed up by Abel (*Phil. Trans.*, 1867, 181). It was at first thought that strong alkalis were beneficial to the stability, but it was gradually found that any benefit which these conferred by removing free acid was outweighed by the decomposition to which they themselves gave rise (Kerckhoff, *J. pr. Chem.*, 1847, **40**, 284; Vohl, *Dingl. polyt. J.*, 1849, **112**, 236; Hadow, T., 1854, **7**, 201; Béchamp, *Compt. rend.*, 1855, **41**, 817; *Ann. Chim. Phys.*, 1856, [iii], **46**, 338; Will, *Ber.*, 1891, **24**, 400; Maquenne, *Ann. Chim. Phys.*, 1891, [vi], **24**, 522; Vignon, *Compt. rend.*, 1898, **127**, 872; *Bull. Soc. chim.*, 1903, [iii], **29**, 507; Nef, *Annalen*, 1899, **309**, 181; Lunge, *Zeitsch. angew. Chem.*, 1901, **14**, 578).

Guttmann, on finding that the prolongation of the heat test by alkalis was largely due to "masking" (*J. Soc. Chem. Ind.*, 1897, **16**, 283), went to the other extreme, and contended against Simon-Thomas that all alkalis were harmful (*Zeitsch. angew. Chem.*, 1897, **10**, 233, 265; 1898, **11**, 1003, 1103; 1899, **12**, 55). The behaviour of nitrocellulose, as shown in the figure (p. 817), indicates that neither of these views is correct. The aim of a stabiliser must be to maintain the concentration of hydrogen ions as near as possible to the point of minimum velocity. In practice, this is effected by using such substances as calcium carbonate for the preservation of wet guncotton. Similarly, the salts of numerous organic acids have been used to stabilise pyroxylin (compare Worden, "Nitrocellulose Industry," p. 598).

Non-hydrolytic Decomposition of Nitric Esters.

Although, as indicated above, hydrolysis is the predominating action in presence of water, nitric esters can also undergo other types of decomposition. For the sake of completeness, these should be briefly referred to. They include both catalytic and non-catalytic reactions.

The non-catalytic decomposition of nitrocellulose is best observed by heating in a vacuum or in a current of dry carbon dioxide (Will's test). Under these conditions, volatile catalysts are

removed continuously, and Will has shown (*Zeitsch. angew. Chem.*, 1901, **14**, 743, 774) that if the guncotton is completely purified from substances that would give rise to non-volatile catalysts, such as sulphuric esters, it reaches a limit state, in which the rate of decomposition sinks to a constant minimum for a given degree of nitration. This has been confirmed by Robertson (*J. Soc. Chem. Ind.*, 1902, **21**, 819), and a similar behaviour has been observed by Robertson for nitroglycerin (T., 1909, **95**, 1241). Measurements in a vacuum give similar results.

This non-catalytic decomposition is extremely slow at ordinary temperatures. Extrapolation shows that at 25° the velocity of evolution of nitrogen from guncotton is approximately 0·00125 milligram per gram per year. In other words, the half-life period of guncotton, if we exclude all catalytic influences, is about 70,000 years (that is, the time necessary for the guncotton to lose half its nitrogen, assuming that the rate of loss is maintained).

Apart from the above, a catalytic decomposition can also occur in presence of nitric peroxide. This has been studied mainly in the case of nitrocellulose. It takes place in absence of moisture and accelerates itself autocatalytically. It consists of an internal oxidation of the nitric ester, aided by atmospheric oxygen, which re-oxidises nitric oxide evolved by the nitrocellulose to nitric peroxide. This is absorbed by the nitrocellulose, and causes further decomposition.

Just in the same way as weak alkalis can be added to protect nitric esters from acid hydrolysis, the catalytic decomposition due to nitric peroxide can be combated by the addition of substances which react with nitric peroxide, such as amines, etc. The analogy extends, however, further than this; for in the same way that the acid hydrolysis has its counterpart in a much more rapid alkaline hydrolysis, so also the nitric peroxide catalysis has its counterpart in a much more rapid action of amines (aminolysis). It was thought originally (Hoitsema, *Zeitsch. angew. Chem.*, 1899, **12**, 705) that amines in general might be added with advantage to take up the nitric peroxide, and so act as stabilisers. It is now known that only very weak bases are permissible; aniline, for instance, is much too strong. Diphenylamine is used in many countries with success as a stabiliser of nitrocellulose propellants, and various other weak bases, such as carbamide, diphenyldimethylcarbamide ("centralite"), diphenyldiethylcarbamide (Claessen, D.R.-P. 909546), nitroguanidine (Flemming, *Zeitsch. angew. Chem.*, 1898, **11**, 1053), and many others, have been proposed. The action of amines of the aniline type is very much more rapid than can be accounted for by the direct hydrolysis due

to the hydroxyl ions, thus showing it to be an entirely different type of reaction.

It should be possible to construct a diagram analogous to that given on p. 817 showing the rate of action of nitric peroxide on the one hand (corresponding with acid hydrolysis), and of amines on the other (corresponding with alkaline hydrolysis). Unfortunately, the data necessary for calculating the point of minimum "aminolysis" are not available, but a rough idea of this point can be obtained from the following comparison:

Base.	Affinity constant (25°).	Action on nitrocellulose.
Benzylamine	$2 \cdot 0 \,.\, 10^{-5}$	Inflamed in a few minutes.
Aniline	$5 \cdot 0 \,.\, 10^{-10}$	
Methylaniline	$2 \cdot 5 \,.\, 10^{-10}$	Rapid action.
Diphenylamine	$5 \cdot 2 \,.\, 10^{-14}$	Probably retard decomposition.
Carbamide	$1 \cdot 5 \,.\, 10^{-14}$	

Instead of the affinity constants, it would probably be more correct to take the "aminolytic" constants, as determined, for instance, by Goldschmidt and Salcher's method (*Zeitsch. physikal. Chem.*, 1899, **29**, 89).

EXPERIMENTAL.

Hydrolysis of Nitroglycerin by Nitric Acid.

Six grams of nitroglycerin were warmed on a water-bath with 400 c.c. of 0·2*N*-nitric acid until all the nitroglycerin had disappeared. A small quantity of dissolved nitroglycerin was extracted with ether. After neutralising the aqueous solution with calcium carbonate, filtering, and evaporating, the residue was extracted with acetone. The acetone gave on evaporation a residue containing no nitrogen, and consisting of glycerol, which was identified by conversion to acrolein, by the boric acid test, and by the colour reaction with pyrogallol. It was further converted to glyceryl tribenzoate (m. p. 70°). Oxalic acid was detected by conversion to calcium oxalate and microscopic examination of its crystals, also by the permanganate test. Distillation of the acidified filtrate showed the presence of volatile acids. The distillate reduced silver nitrate and mercuric chloride (formic acid). After elimination of the formic acid by mercuric chloride, the filtrate gave a precipitate on boiling with ferric chloride (probably acetic acid). The solution gave a red colour with Schiff's reagent, but gave no precipitate with phenylhydrazine.

Partial Hydrolysis of Nitroglycerin with Nitric Acid.

In this case, the same quantities were used, but the hydrolysis was interrupted when about two-thirds of the nitroglycerin had

disappeared. The aqueous layer was separated and extracted with ether. The residue obtained on evaporation of the ether was purified by dissolving in a limited quantity of water and removing the residual oil. The aqueous solution was again extracted with ether, and the ether evaporated. The residue contained N = 14·65, whilst glyceryl dinitrate requires N = 15·39 per cent.; the product must therefore have retained some mononitrate, which is difficult to separate completely from the dinitrate. It was benzoylated with some difficulty, and the benzoyl derivative melted at 63° and contained N = 10·03. The quantity was insufficient for further purification, but the substance was evidently the benzoyl derivative of glyceryl $\alpha\alpha'$-dinitrate, which in the pure state melts at 67° and contains N = 9·79 per cent. Glyceryl mononitrate was obtained only in small quantity and in an impure state.

Hydrolysis of Nitroglycerin by Phosphoric Acid.

The solution obtained on hydrolysis was neutralised with lime, and filtered from the calcium phosphate which separated. The filtrate yielded on evaporation a syrup, which contained calcium nitrate, and also a soluble calcium salt, from which phosphoric acid and glycerol were obtained. It appears, therefore, to be the calcium salt of glycerophosphoric acid. Further examination of the products of the hydrolysis showed that oxalic acid was absent, and formic acid was present only in very small quantity. Practically no oxidation of the glycerol took place.

Hydrolysis of Glyceryl Dinitrate.

In order to ascertain whether the hydrolysis was accompanied by reduction of the nitric acid, a solution of glyceryl dinitrate in nitric acid was maintained at 80°. Separate bottles, each containing 50 c.c. of solution, were used, and these were withdrawn at intervals and a portion titrated. To ascertain whether reduction of the nitric acid occurred, estimations of nitrous acid were also made.

Concentration of Glyceryl Dinitrate = 0·060. *Temperature* = 80°.

Time (hours).	Concentration of acid (gr. equiv.).	Nitrous acid (mgr.).	Time (hours).	Concentration of acid (gr. equiv.).	Nitrous acid (mgr.).
—	0·200	0·00418	28	0·264	0·0028
4	0·211	—	36	0·275	0·0021
8	0·221	—	44	0·278	0·0084
12	0·232	—	66	0·302	0·0135
16	0·243	—	114	0·312	—
20	0·245	—	—	—	—

The increase in the acidity corresponds with the decomposition of 93 per cent. of the glyceryl dinitrate to glycerol and nitric acid. Very little reduction of nitric acid occurred, as shown by the low proportion of nitrous acid.

In order to ascertain whether the solution contained any acids other than nitric acid, it was extracted with ether to remove unchanged glyceryl dinitrate, and then subjected to reduction. The ammonia was estimated and recalculated to nitric acid. Oxalic and formic acid were also tested for.

	Original (gr. equiv.).	After 114 hours (gr. equiv.).
Nitric acid (NH_3 method) ...	0·1978	0·3005
Formic acid	—	0·0056
Oxalic acid	—	—
Total	—	0·3061
Total acid by titration	0·2000	0·3124

Any other organic acids must thus form less than 2 per cent. of the total acid present.

Formic and Oxalic Acids in Hydrolysis of Cordite.

Several methods were tried for the estimation of formic acid, and the following method was found to be the best. The solution containing formic acid is boiled with a known amount of silver nitrate in the presence of barium carbonate for two hours; excess of standard ammonium thiocyanate solution is then added and the mixture allowed to remain for ten minutes. The solution is filtered, and the excess of thiocyanate estimated in the filtrate by silver nitrate solution. A control test is carried out simultaneously. Tests on known small quantities of formic acid gave satisfactory results.

For the estimations on cordite, 50 grams of the ground cordite were extracted with 100 c.c. of water for two hours on a steam-bath. After filtration and washing, the solution was extracted with ether, neutralised, and evaporated to a small bulk. It was then rendered slightly acid with nitric acid and warmed. Ammonia was added in slight excess and the solution filtered. Calcium nitrate was added and the liquid allowed to remain overnight. Any calcium oxalate was filtered off, dissolved in sulphuric acid, and estimated by permanganate. The filtrate was acidified slightly with sulphuric acid and distilled to recover the formic acid, which was then estimated as above. It was found by separate experiments that no formic acid was destroyed by the nitric acid present.

Cordite.	Formic acid (per cent.).	Oxalic acid (per cent.).
(a)	0·0068	0·0022
(b)	0·0048	0·0019
(c)	0·030	—
(d)	0·037	—
(e)	0·0039	—
(a) After six months at 46° in a wet atmosphere	0·0108	0·0115
(a) After approx. 500 hours at 80°	0·0287	0·239

Minimum Velocity of Hydrolysis of Guncotton.

If the concentration of hydrogen and hydroxyl ions be repr sented by H and OH, and the velocity-coefficients for acid ar alkaline hydrolysis by C_1 and C_2 respectively, the minimum velocit will be reached when $d(C_1H + C_2OH) = 0$ or $d\left(C_1H + C_2\frac{K}{H}\right) = 0$, whe K is the water constant $H \times OH$.

$$\text{Now } d\left(C_1H + C_2\frac{K}{H}\right) = C_1dH - \frac{C_2KdH}{H^2} = dH\left(C_1 - \frac{C_2K}{H^2}\right) = dH\left(C_1 - C_2\frac{OH}{H}\right)$$

Experiment shows that the hydrolysis continues to take pla through the neutral point, the alkalinity disappearing and acidi being developed; hence dH never becomes equal to zero. Fro this it follows that $\frac{C_1}{C_2} = \frac{OH}{H}$.

The concentrations at the point of minimum velocity are given l

$$OH = \sqrt{\frac{KC_1}{C_2}};\ H = \sqrt{\frac{KC_2}{C_1}}.$$

Data for the velocity-constants are given by Silberrad ar Farmer (T., 1906, **89**, 1759). The total velocity of hydrolysis made up of the sum of the velocities due to hydrogen and hydrox ions. The following table shows the velocities in the neighbou hood of the minimum point.

Velocities of Hydrolysis of Guncotton at Low Concentrations Hydrogen Ions. (Equivalent per litre per hour. At 37·8°.)

H-ions conc. (10^{-8})	OH-ions conc. (10^{-9})	Velocity. Due to H-ions. (10^{-9})	Due to OH-ions. (10^{-9})	Total. (10^{-9})
0·5	58·0	0·44	24·00	24·44
1·0	29·0	0·87	12·00	12·87
2·0	14·5	1·74	6·00	7·74
3·0	9·7	2·61	4·00	6·61
3·7	7·8	3·25	3·25	6·50
5·0	5·8	4·35	2·40	6·75
10·0	2·9	8·70	1·20	9·90
20·0	1·45	17·40	0·60	18·00

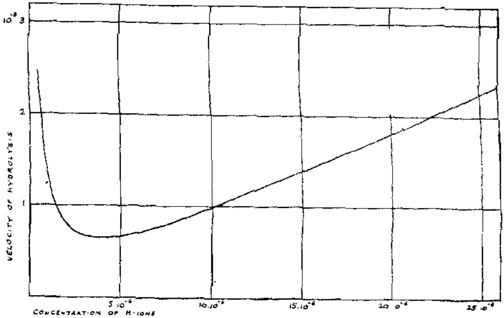
The course of the hydrolysis is shown in the figure. Tl minimum velocity is seen to lie distinctly on the acid side of tl

neutral point. The acidity is comparable with that of a 0·1*N*-solution of phenol.

Decomposition of Nitrocellulose in the Presence of Amines.

To illustrate the decomposing action of organic bases as compared with alkaline salts, the following examples may be given. Fifty grams of nitrocellulose were enclosed in a vessel of 100 c.c. capacity, and the alteration of gas volume was measured by a gas

Velocity of hydrolysis of nitrocellulose at 37·8° (equivalent per litre per hour).



burette at the ordinary temperature (mean = 16°). The contraction is due to the formation of nitric oxide, which absorbs oxygen from the air. In each case, 5 per cent. of admixture was taken.

Alteration in Gas Volume at 16° (c.c. corr.).

Days.	2·7.	4·6.	7·0.	12.	18.	20.	33.
Sodium carbonate	—	+0·15	+0·10	−0·05	−0·10	−0·25	−0·35
Methylaniline ...	−4·6	−5·65	−6·80	−8·30	−9·90	−10·45	−11·85

The nitrocellulose itself showed only a very slight contraction. When it was mixed with diphenylamine, the contraction was also very slight. On attempting to make measurements with benzylamine, the decomposition was so rapid that the nitrocellulose inflamed in a few minutes.

Affinity Constant of Diphenylamine.—This did not lend itself to the ordinary methods of determination, but can be deduced from the solubility of diphenylamine in water and in acid.

	Gram per litre.	Gram-molecule per litre.
Solubility in water at 25°	0·0462	0·0002734
	0·0474	0·0002805
„ „ 0·211*N*-HCl at 25°	0·0855	0·000507

The concentration of hydrogen ions in $0{\cdot}211N$-hydrochloric acid is 0·192. Assuming the diphenylamine hydrochloride at the above high dilution to be completely ionised, the hydrolytic constant

$$\frac{\text{acid} \times \text{base}}{\text{salt}} = \frac{0{\cdot}1917 \times 0{\cdot}000277}{0{\cdot}000230} = 0{\cdot}230$$

and the affinity constant of the free base is equal to $5{\cdot}2 \times 10^{-1}$ taking the ionisation of water as $1{\cdot}09 \times 10^{-7}$.

Summary.

The different forms of decomposition of nitric esters can b classified as follows:

(1) *Decomposition of the pure ester.*

(2) Accelerated decomposition.

(*a*) Hydrolysis (followed by internal oxidation):

(i) by acids (slow but autocatalytically accelerated);

(ii) by alkalis (relatively rapid).

(*b*) Internal oxidation in absence of water:

(i) by nitric peroxide (slow but autocatalytical accelerated);

(ii) by amines, etc. (relatively rapid).

The hydrolytic decomposition passes through the followi phases:

(i) Incipient ester hydrolysis.

(ii) Internal oxidation, possibly to an alcohol peroxi (although this is speculative).

(iii) Formation of an aldehyde.

(iv) Decomposition to hydroxy-acids.

When the conditions are such that the alcohol is protected fr oxidation, it is readily regenerated as such on hydrolysis, tl showing that the first stage in the decomposition is a true es hydrolysis of the normal type. The hydrolysis is shown resemble that of other esters in its general relationship betw velocity and concentration of hydrogen or hydroxyl ions, and bearing of this relationship on the stabilisation of nitric ester shown.

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